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(54) **Nonaqueous secondary battery.**

(57) A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt is disclosed, in which the negative electrode active material contains (1) a compound capable of intercalating and deintercalating lithium comprising an atom of the group IIIB, IVB or VB of the periodic table, (2) an amorphous compound containing at least two atoms selected from the elements of the groups IIIB, IVB, and VB of the periodic table, (3) a compound capable of intercalating and deintercalating lithium containing at least one of the atoms of the group IIIB, IVB, and VB of the periodic table and fluorine, or (4) a compound of the metal of the group IIIB, IVB or VB of the periodic table, Zn, or Mg which is capable of intercalating and deintercalating lithium. The nonaqueous secondary battery of the invention exhibits improved charge and discharge characteristics and improved safety.

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FIELD OF THE INVENTION

This invention relates to a nonaqueous secondary battery having improved charge and discharge cycle characteristics and improved safety.

BACKGROUND OF THE INVENTION

Negative electrode active materials for nonaqueous secondary batteries typically include metallic lithium and lithium alloys. The problem associated with these active materials is that metallic lithium grows dendritically during charging and discharging to cause an internal short circuit, involving a danger of ignition because of high activity of the dendrital metal per se. To solve the problem, a calcined carbonaceous material capable of intercalating and deintercalating lithium has recently been put to practical use. However, since the carbonaceous material has electrical conductivity by itself, metallic lithium is sometimes precipitated on the carbonaceous material at the time of an overcharge or a rapid charge. It eventually follows that lithium grows dendritically thereon. This problem has been dealt with by altering a charger or reducing the amount of the positive electrode active material to prevent an overcharge. Where the latter solution is adopted, however, the limited amount of the active material leads to a limited discharge capacity. Further, the carbonaceous material has a relatively low density and therefore a low capacity per unit volume. Thus, the discharge capacity is limited by both the amount of the active material and the capacity per unit volume.

In addition to metallic lithium, lithium alloys and the above-mentioned carbonaceous material, negative electrode active materials so far proposed include TiS_2 and LiTiS_2 which are capable of intercalating and deintercalating lithium (U.S. Patent 3,983,476); transition metal oxides having a rutile structure, such as WO_2 (U.S. Patent 4,198,476), spinel compounds, such as $\text{Li}_x\text{Fe}(\text{Fe}_2)\text{O}_4$ (JP-A-58-220362, the term "JP-A" as used herein means an "unexamined published Japanese patent application"); a electrochemically synthesized lithium compound of Fe_2O_3 (U.S. Patent 4,464,447); a lithium compound of Fe_2O_3 (JP-A-3-112070); Nb_2O_5 (JP-B-62-59412 (the term "JP-B" as used herein means an "examined published Japanese patent application") and JP-A-2-82447); FeO , Fe_2O_3 , Fe_3O_4 , CoO , Co_2O_3 , and Co_3O_4 (JP-A-3-291862); amorphous V_2O_5 (JP-A-4-223061); and transition metal oxides having their basic crystal structure changed by intercalation of a lithium ion (EP 567149). Any of these known compounds has a high oxidation-reduction potential, failing to provide a nonaqueous secondary battery having a discharge potential as high as 3 V and a high capacity.

SnO_2 or Sn compounds are used as an active material of lithium batteries as in $\text{Li}_{1.03}\text{Co}_{0.95}\text{Sn}_{0.04}\text{O}_2$ as a secondary battery positive electrode active material (EP 86-106301); SnO_2 -added V_2O_5 as a secondary battery positive electrode active material (JP-A-2-158056); SnO_2 -added $\alpha\text{-Fe}_2\text{O}_3$ (preferred SnO_2 content: 0.5 to 10 mol%) as a secondary battery negative electrode active material (JP-A-62-219465); and SnO_2 as a primary battery positive electrode active material (Denki Kagaku oyobi Kogyo Butsuri Kagaku, Vol. 46, No. 7, p. 407 (1978)). With reference to the use of SnO_2 or Sn compounds as an electrochromic electrode, it is known that SnO_2 is capable of reversible intercalation of an Li ion (see Journal of Electrochemical Society, Vol. 140, No. 5, L81 (1993) and that a film comprising InO_2 doped with 8 mol% of Sn (i.e., ITO) is capable of reversible intercalation of an Li ion (see Solid State Ionics, Vols. 28-30, p. 1733 (1988)). However, the electrode useful in an electrochromic system should be transparent, the active material is used in the form of a thin film formed by, for example, vacuum evaporation, and the electrode usually works at a considerably low current differing from the practical range of batteries. For example, Solid State Ionics, supra, shows a working current of 1 μA to 30 $\mu\text{A}/\text{cm}^2$ as an experimental example.

Known positive electrode active materials include spinel compounds disclosed in JP-B-4-30146 and cobalt oxide disclosed in JP-B-63-59507.

It is possible to combine these positive electrode active materials with an oxide mainly comprising Sn as a negative electrode active material to provide a nonaqueous secondary battery having a high discharge potential, a high capacity, improved charge and discharge cycle characteristics, and increased safety. Yet, the charge and discharge cycle characteristics are still unsatisfactory as described above, and it has been keenly demanded to further improve charge and discharge cycle characteristics.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a nonaqueous secondary battery having improved charge and discharge cycle characteristics, a high discharge potential, a high discharge capacity, and increased safety.

The above object of the present invention is accomplished by a nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt, in which (1) the negative electrode active material contains at least one compound capable of intercalating and deintercalating lithium mainly comprising an atom of the group IIIB, IVB or VB of the periodic table, (2) the negative electrode active material mainly comprises an amorphous compound containing at least two atoms selected from the elements of the groups IIIB, IVB, and VB of the periodic table, (3) the negative electrode active material is a compound capable of intercalating and deintercalating lithium containing at least one of the atoms of the group IIIB, IVB, and VB of the periodic table and fluorine, or (4) the negative electrode active material contains at least one compound of the atom of the group IIIB, IVB or VB of the periodic table, Zn, or Mg which is capable of intercalating and deintercalating lithium.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is the X-ray diffraction pattern of compound D-1-A prepared in Synthesis Example D-1.

Fig. 2 is a cross section of a coin battery prepared in Examples, wherein 1 indicates a negative electrode sealing plate, 2 indicates a negative electrode active material mixture pellet, 3 indicates a separator, 4 indicates a positive electrode active material mixture pellet, 5 indicates a collector, 6 indicates a positive electrode case, and 7 indicates a gasket.

Fig. 3 is a cross section of a cylindrical battery prepared in Examples, wherein 8 indicates a positive electrode sheet, 9 indicates a negative electrode sheet, 10 indicates a separator, 11 indicates a battery case, 12 indicates a battery cover, 13 indicates a gasket, and 14 indicates a safety valve.

DETAILED DESCRIPTION OF THE INVENTION

The terminology "negative electrode active material precursor" as used herein is explained below. The inventors have found that SnO having an α -PbO structure, SnO₂ having a rutile structure, and the like do not act by themselves as a negative electrode active material of a secondary battery but change their crystal structure on intercalation of lithium to act as a reversible negative electrode active material. That is, the charge and discharge efficiency of the first cycle is as low as about 80% or 60%. Thus, the starting material, such as α -PbO-structure SnO or rutile-structure SnO₂, namely, a compound before lithium intercalation is called a "negative electrode active material precursor".

The negative electrode active material according to the present invention can be obtained by electrochemically intercalating a lithium ion into, for example, an oxide, an active material precursor. Lithium ion intercalation is conducted until the basic structure of the oxide is changed (for example, until the X-ray diffraction pattern changes) and also until the thus changed basic structure of the Li ion-containing oxide undergoes substantially no change during charging and discharging (for example, the X-ray diffraction pattern does not change substantially). The change in basic structure means change from a certain crystal structure to a different crystal structure or from a crystal structure to an amorphous structure.

Where the compound represented by formulae (I) to (V) of the present invention described in later is used as a negative electrode active material precursor, it was found that intercalation of lithium does not cause reduction of the respective metal (an alloy with lithium). This can be confirmed from the fact that (1) observation under a transmission electron microscope reveals no precipitation of a metal (especially no precipitation of a dendrite), (2) the potential of lithium intercalation/deintercalation via a metal is different from that of the oxide, and (3) the lithium deintercalation loss with respect to lithium intercalation in SnO was about 1 equivalent, which does not agree with a loss of 2 equivalents in the case where metallic tin is generated. Since the potential of an oxide is similar to that of a currently employed calcined carbonaceous compound, it is assumed that the bonding state of lithium is neither mere ionic bonding nor mere metallic bonding, similarly to a calcined carbonaceous compound. Accordingly, the negative electrode active material of the present invention is obviously different from conventional lithium alloys.

It is preferable that the active material precursor which can be used in the present invention is substantially amorphous at the time of battery assembly (before lithium ion intercalation). The term "substantially amorphous" as used herein means that an X-ray diffraction pattern using CuK α rays shows a broad scattering band with peaks between 20° and 40° in terms of 2 θ and may contain diffraction assigned to a crystalline structure.

The maximum intensity of the peaks assigned to the crystalline structure appearing between 2 θ = 40° and 70° is preferably not higher than 500 times, still preferably not higher than 100 times, still more preferably not higher than 5 times, the intensity of the peak of the broad scattering band appearing between 2 θ = 20° and 40°. It is the most preferred that the pattern exhibits no crystalline diffraction spectrum.

Also, it is preferred that the active material precursor is substantially amorphous at the time of intercalating lithium ion.

In the present invention, either the active material precursor or the active material can be used as a negative electrode. Hereinafter, cases are met in which they are represented as an active material.

5 The metals of the groups IIIB to VB of the periodic table which can be used in the present invention include B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Sb, and Bi, preferably B, Al, Si, Ge, Sn, Pb, P, As, Sb, and Bi, still preferably Al, Si, Ge, Sn, Pb, As, and Sb or B, Al, Si, Ge, Sn, and P.

10 Examples of the negative electrode active material according to the present invention include GeO , GeO_2 , SnO , SiO , SnO_2 , PbO , PbO_2 , Pb_2O_3 , Pb_3O_4 , Sb_2O_3 , Sb_2O_4 , Sb_2O_5 , Bi_2O_3 , Bi_2O_4 , and Bi_2O_6 , and non-stoichiometrical compounds of these oxides.

Preferred of them are SnO , SnO_2 , GeO , and GeO_2 , with SnO and SnO_2 being particularly preferred. α - PbO -structure SnO , rutile-structure SnO_2 , GeO , and rutile-structure GeO_2 are preferred, with α - PbO -structure SnO and rutile-structure SnO_2 being particularly preferred.

Still preferred negative electrode active materials are represented by formula (I):

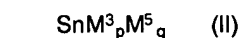


wherein M^1 and M^2 , which are different from each other, each represent at least one of Si, Ge, Sn, Pb, P, B, Al, As, and Sb, preferably at least one of Si, Ge, Sn, Pb, P, B, Al, and Sb, still preferably at least one of Si, Ge, Sn, Pb, P, B, and Al; M^4 represents at least one of O, S, Se, and Te, preferably at least one of O and S, still preferably O; p represents a number exceeding 0 and not exceeding 10, generally from 0.001 to 10, preferably from 0.01 to 5, still preferably from 0.01 to 2; and q represents a number of from 1 to 50, preferably 1 to 26, still preferably 1.02 to 6.

25 Also, preferred are those of formula (I) in which M^1 and M^2 are different from each other; M^1 represents at least one of Ge, Sn, Pb, Sb, and Bi; M^2 represents at least one atom of the groups IIIB, IVB, and VB of the periodic table (exclusive of Ge, Sn, Pb, Sb, and Bi when M^1 represents each of these); p represents a number of from 0.001 to 1; and M^4 and q have the same meanings as defined in formula (I) above.

The valency of M^1 or M^2 in formula (I) is not particularly limited and may be either a single valency or a mixed valency. The M^2 to M^1 ratio may vary continuously within a range of from more than 0 up to 10 molar equivalents. The amount of M^4 , represented by q in formula (I), continuously varies accordingly.

30 Of the compounds of formula (I), preferred are those in which M^1 is Sn, i.e., compounds represented by formula (II):



wherein M^3 represents at least one of Si, Ge, Pb, P, B, Al, As, and Sb, preferably at least one of Si, Ge, Pb, P, B, Al, and Sb, still preferably at least one of Si, Ge, Pb, P, B, and Al; M^5 represents at least one of O and S, preferably O; p represents a number exceeding 0 and not exceeding 10, generally from 0.001 to 10, preferably from 0.01 to 5, more preferably a number of from 0.01 to 1.5, still preferably from 0.7 to 1.5; and q represents a number of from 1.0 to 50, preferably from 1.0 to 26, still preferably from 1.02 to 6.

Still preferred of the compounds represented by formula (II) are those represented by formula (III):



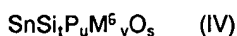
45 wherein M^3 is as defined above, preferably Si; r represents a number of exceeding 0 and not exceeding 5.0, generally from 0.01 to 5.0, preferably a number of from 0.01 to 1.5, still preferably from 0.7 to 1.5; and s represents a number of from 1.0 to 26, preferably from 1.02 to 6.

Examples of the compounds represented by formula (II) or (III) are $\text{SnSi}_{0.01}\text{O}_{1.02}$, $\text{SnGe}_{0.01}\text{O}_{1.02}$, $\text{SnPb}_{0.01}\text{O}_{1.02}$, $\text{SnP}_{0.01}\text{O}_{1.025}$, $\text{SnB}_{0.01}\text{O}_{1.015}$, $\text{SnAl}_{0.01}\text{O}_{1.015}$, $\text{SnSi}_{0.01}\text{O}_{2.02}$, $\text{SnGe}_{0.01}\text{O}_{2.02}$, $\text{SnPb}_{0.01}\text{O}_{2.02}$, $\text{SnP}_{0.01}\text{O}_{2.025}$, $\text{SnB}_{0.01}\text{O}_{2.015}$, $\text{SnSi}_{0.05}\text{O}_{1.1}$, $\text{SnGe}_{0.05}\text{O}_{1.1}$, $\text{SnPb}_{0.05}\text{O}_{1.1}$, $\text{SnP}_{0.05}\text{O}_{1.125}$, $\text{SnB}_{0.05}\text{O}_{1.075}$, $\text{SnSi}_{0.05}\text{O}_{2.1}$, $\text{SnGe}_{0.05}\text{O}_{2.1}$, $\text{SnPb}_{0.05}\text{O}_{2.1}$, $\text{SnP}_{0.05}\text{O}_{2.125}$, $\text{SnB}_{0.05}\text{O}_{2.075}$, $\text{SnSi}_{0.1}\text{O}_{1.2}$, $\text{SnGe}_{0.1}\text{O}_{1.2}$, $\text{SnPb}_{0.1}\text{O}_{1.2}$, $\text{SnP}_{0.1}\text{O}_{1.25}$, $\text{SnB}_{0.1}\text{O}_{1.15}$, $\text{SnSi}_{0.1}\text{O}_{2.2}$, $\text{SnGe}_{0.1}\text{O}_{2.2}$, $\text{SnPb}_{0.1}\text{O}_{2.2}$, $\text{SnP}_{0.1}\text{O}_{2.25}$, $\text{SnB}_{0.1}\text{O}_{2.15}$, $\text{SnSi}_{0.2}\text{O}_{1.4}$, $\text{SnGe}_{0.2}\text{O}_{1.4}$, $\text{SnPb}_{0.2}\text{O}_{1.4}$, $\text{SnP}_{0.2}\text{O}_{1.5}$, $\text{SnB}_{0.2}\text{O}_{1.3}$, $\text{SnSi}_{0.2}\text{O}_{2.4}$, $\text{SnGe}_{0.2}\text{O}_{2.4}$, $\text{SnPb}_{0.2}\text{O}_{2.4}$, $\text{SnP}_{0.2}\text{O}_{2.5}$, $\text{SnB}_{0.2}\text{O}_{2.3}$, $\text{SnSi}_{0.3}\text{O}_{1.6}$, $\text{SnGe}_{0.3}\text{O}_{1.6}$, $\text{SnPb}_{0.3}\text{O}_{1.6}$, $\text{SnP}_{0.3}\text{O}_{1.75}$, $\text{SnB}_{0.3}\text{O}_{1.45}$, $\text{SnSi}_{0.3}\text{O}_{2.6}$, $\text{SnGe}_{0.3}\text{O}_{2.6}$, $\text{SnPb}_{0.3}\text{O}_{2.6}$, $\text{SnP}_{0.3}\text{O}_{2.75}$, $\text{SnB}_{0.3}\text{O}_{2.45}$, $\text{SnSi}_{0.7}\text{O}_{2.4}$, $\text{SnGe}_{0.7}\text{O}_{2.4}$, $\text{SnPb}_{0.7}\text{O}_{2.4}$, $\text{SnP}_{0.7}\text{O}_{2.75}$, $\text{SnB}_{0.7}\text{O}_{2.05}$, $\text{SnSi}_{0.8}\text{O}_{2.6}$, $\text{SnGe}_{0.8}\text{O}_{2.6}$, $\text{SnPb}_{0.8}\text{O}_{2.6}$, $\text{SnP}_{0.8}\text{O}_3$, $\text{SnB}_{0.8}\text{O}_{2.2}$, SnSiO_3 , SnGeO_3 , SnPbO_3 , $\text{SnPO}_{3.5}$, $\text{SnBO}_{2.5}$, $\text{SnSi}_{1.2}\text{O}_{3.4}$, $\text{SnGe}_{1.2}\text{O}_{3.4}$, $\text{SnPb}_{1.2}\text{O}_{3.4}$, $\text{SnP}_{1.2}\text{O}_4$, $\text{SnB}_{1.2}\text{O}_{2.8}$, $\text{SnSi}_{1.5}\text{O}_4$, $\text{SnGe}_{1.5}\text{O}_4$, $\text{SnPb}_{1.5}\text{O}_4$, $\text{SnP}_{1.5}\text{O}_{4.75}$, $\text{SnB}_{1.5}\text{O}_{3.25}$, SnSi_2O_5 , SnGe_2O_5 , SnPb_2O_5 , SnP_2O_6 , SnB_2O_4 , SnSi_2O_6 , SnGe_2O_6 , SnPb_2O_6 , SnP_2O_7 , SnB_2O_5 , SnSiS_3 .

SnSiSe_3 , SnSiTe_3 , $\text{SnPS}_{3.5}$, $\text{SnPSe}_{3.5}$, $\text{SnPTe}_{3.5}$, $\text{SnBS}_{2.5}$, $\text{SnBSe}_{2.5}$, $\text{SnBTe}_{2.5}$, $\text{SnP}_{0.8}\text{O}_3$, $\text{SnB}_{0.8}\text{O}_{2.2}$, and $\text{SnSi}_{0.25}\text{BO}_3$.

The valency of Sn and M^3 in formula (II) or (III) is not particularly limited and may be a single valency or a mixed valency. The ratio of M^3 to Sn in the compound of formula (II) may vary continuously within a range of from 0.01 to 10 molar equivalents. Accordingly, the amount of M^5 , represented by q in formula (II), varies continuously. Similarly, the ratio of M^3 to Sn in the compound of formula (III) may vary continuously within a range of from 0.01 to 5.0 molar equivalents. Accordingly, the amount of oxygen, represented by s in formula (III), varies continuously.

Of the compounds of formula (III), preferred are those represented by formula (IV):



Of the compounds of formula (IV), preferred are those represented by formula (V):



In formulae (IV) and (V), M^6 represents at least one of Ge, B, Al, and Pb, preferably at least one of Ge, Al, and B, still preferably Al; M^7 represents at least one of Ge, B, and P; t represents a number exceeding 0 and not exceeding 2.0 (preferably not exceeding 1.5), generally from 0.01 to 2.0, preferably from 0.01 to 1.5; u represents a number of from 0.01 to 4.0, preferably from 0.01 to 3.5; v represents a number exceeding 0 and not exceeding 2.0 (preferably not exceeding 1.5), generally from 0.01 to 2.0, preferably from 0.01 to 1.5; w represents a number exceeding 0 to not exceeding 2.0, generally from 0.01 to 2.0; and s represents a number of from 1.0 to 26, preferably from 1.02 to 10.

Specific but non-limiting examples of the oxides represented by formula (IV) or (V) are

$\text{SnSi}_{0.25}\text{B}_{0.2}\text{P}_{0.2}\text{O}_3$, $\text{SnSi}_{0.5}\text{B}_{0.2}\text{P}_{0.2}\text{O}_3$, $\text{SnSi}_{0.9}\text{P}_{0.1}\text{O}_{2.25}$, $\text{SnSi}_{0.8}\text{P}_{0.2}\text{O}_{3.1}$, $\text{SnSi}_{0.7}\text{P}_{0.3}\text{O}_{2.75}$, $\text{SnSi}_{0.5}\text{P}_{0.5}\text{O}_{3.25}$, $\text{SnSi}_{0.3}\text{P}_{0.7}\text{O}_{3.35}$, $\text{SnSi}_{0.2}\text{P}_{0.8}\text{O}_{3.4}$, $\text{SnSi}_{0.5}\text{P}_{0.1}\text{O}_{2.25}$, $\text{SnSi}_{0.1}\text{Ge}_{0.1}\text{P}_{0.9}\text{O}_{3.65}$, $\text{SnSi}_{0.2}\text{Ge}_{0.1}\text{P}_{0.7}\text{O}_{3.35}$, $\text{SnSi}_{0.6}\text{Ge}_{0.4}\text{P}_{0.1}\text{O}_{3.25}$, $\text{SnSi}_{0.6}\text{Ge}_{0.2}\text{P}_{0.2}\text{O}_{3.1}$, $\text{SnSi}_{0.7}\text{Ge}_{0.1}\text{P}_{0.2}\text{O}_{3.1}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{P}_{0.1}\text{O}_{3.05}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{P}_{0.3}\text{O}_{3.55}$, $\text{SnSiGe}_{0.1}\text{P}_{0.1}\text{O}_{3.45}$, $\text{SnSiGe}_{0.2}\text{P}_{0.2}\text{O}_{3.9}$, $\text{SnSiGe}_{0.1}\text{P}_{0.2}\text{O}_{3.7}$, $\text{SnSi}_{0.1}\text{Al}_{0.1}\text{P}_{0.9}\text{O}_{3.6}$, $\text{SnSi}_{0.3}\text{Al}_{0.1}\text{P}_{0.7}\text{O}_{3.5}$, $\text{SnSi}_{0.6}\text{Al}_{0.3}\text{P}_{0.1}\text{O}_{2.9}$, $\text{SnSi}_{0.6}\text{Al}_{0.2}\text{P}_{0.2}\text{O}_3$, $\text{SnSi}_{0.6}\text{Al}_{0.1}\text{P}_{0.3}\text{O}_{3.1}$, $\text{SnSi}_{0.8}\text{Al}_{0.1}\text{P}_{0.1}\text{O}_3$, $\text{SnSi}_{0.8}\text{Al}_{0.1}\text{P}_{0.2}\text{O}_{3.25}$, $\text{SnSi}_{0.8}\text{Al}_{0.2}\text{P}_{0.2}\text{O}_{3.4}$, $\text{SnSi}_{0.7}\text{Al}_{0.2}\text{P}_{0.3}\text{O}_{3.45}$, $\text{SnSi}_{0.4}\text{Al}_{0.2}\text{P}_{0.6}\text{O}_{3.6}$, $\text{SnSiAl}_{0.2}\text{P}_{0.4}\text{O}_{3.5}$, $\text{SnSiAl}_{0.1}\text{P}_{0.1}\text{O}_{3.4}$, $\text{SnSiAl}_{0.2}\text{P}_{0.2}\text{O}_{3.8}$, $\text{SnSiAl}_{0.1}\text{P}_{0.2}\text{O}_{3.65}$, $\text{SnSi}_{0.1}\text{B}_{0.1}\text{P}_{0.9}\text{O}_{3.6}$, $\text{SnSi}_{0.3}\text{B}_{0.1}\text{P}_{0.7}\text{O}_{3.5}$, $\text{SnSi}_{0.6}\text{B}_{0.3}\text{P}_{0.1}\text{O}_{2.9}$, $\text{SnSi}_{0.6}\text{B}_{0.3}\text{P}_{0.1}\text{O}_{2.9}$, $\text{SnSi}_{0.6}\text{B}_{0.1}\text{P}_{0.3}\text{O}_{3.1}$, $\text{SnSi}_{0.6}\text{B}_{0.1}\text{P}_{0.1}\text{O}_3$, $\text{SnSi}_{0.8}\text{B}_{0.1}\text{P}_{0.3}\text{O}_{3.5}$, $\text{SnSiB}_{0.1}\text{P}_{0.1}\text{O}_{3.4}$, $\text{SnSiB}_{0.2}\text{P}_{0.2}\text{O}_{3.8}$, $\text{SnSiB}_{0.1}\text{P}_{0.2}\text{O}_{3.65}$, $\text{SnSi}_{0.1}\text{Pb}_{0.1}\text{P}_{0.9}\text{O}_{3.6}$, $\text{SnSi}_{0.3}\text{Pb}_{0.1}\text{P}_{0.7}\text{O}_{3.5}$, $\text{SnSi}_{0.6}\text{Pb}_{0.3}\text{P}_{0.1}\text{O}_{2.9}$, $\text{SnSi}_{0.6}\text{Pb}_{0.2}\text{P}_{0.2}\text{O}_3$, $\text{SnSi}_{0.6}\text{Pb}_{0.1}\text{P}_{0.3}\text{O}_{3.1}$, $\text{SnSi}_{0.8}\text{Pb}_{0.1}\text{P}_{0.1}\text{O}_3$, $\text{SnSi}_{0.8}\text{Pb}_{0.1}\text{P}_{0.3}\text{O}_{3.5}$, $\text{SnSiPb}_{0.1}\text{P}_{0.1}\text{O}_{3.4}$, $\text{SnSiPb}_{0.2}\text{P}_{0.2}\text{O}_{3.8}$, $\text{SnSiPb}_{0.1}\text{P}_{0.2}\text{O}_{3.65}$, $\text{SnPAl}_{0.1}\text{O}_{3.65}$, $\text{SnPAl}_{0.3}\text{O}_{3.95}$, $\text{SnP}_{0.8}\text{Al}_{0.1}\text{O}_{3.15}$, $\text{SnP}_{0.8}\text{Al}_{0.3}\text{O}_{2.45}$, $\text{SnP}_{0.5}\text{Al}_{0.1}\text{O}_{2.4}$, and $\text{SnP}_{0.5}\text{Al}_{0.3}\text{O}_{2.7}$. The valency of Sn and M^6 are not particularly limited and may be a single valency or a mixed valency. The ratio of M^6 to Sn may vary continuously within a range of from 0 to 2 molar equivalents, and the amount of oxygen continuously varies accordingly.

Additional examples of the compounds represented by formulae (I) to (V) are shown below.

$\text{SnSi}_{0.1}\text{Ge}_{0.1}\text{Pb}_{0.1}\text{O}_{2.6}$, $\text{SnSi}_{0.2}\text{Ge}_{0.1}\text{O}_{2.6}$, $\text{SnSi}_{0.2}\text{Pb}_{0.1}\text{O}_{2.6}$, $\text{SnGe}_{0.2}\text{Si}_{0.1}\text{O}_{2.6}$, $\text{SnPb}_{0.2}\text{Si}_{0.1}\text{O}_{2.6}$, $\text{SnGe}_{0.2}\text{Pb}_{0.1}\text{O}_{2.6}$, $\text{SnPb}_{0.2}\text{Ge}_{0.1}\text{O}_{2.6}$, $\text{SnSi}_{0.9}\text{Ge}_{0.1}\text{O}_3$, $\text{SnSi}_{0.8}\text{Ge}_{0.2}\text{O}_3$, $\text{SnSi}_{0.5}\text{Ge}_{0.5}\text{O}_3$, $\text{SnSi}_{0.9}\text{Pb}_{0.1}\text{O}_3$, $\text{SnSi}_{0.8}\text{Pb}_{0.2}\text{O}_3$, $\text{SnSi}_{0.5}\text{Pb}_{0.5}\text{O}_3$, $\text{SnGe}_{0.9}\text{Si}_{0.1}\text{O}_3$, $\text{SnGe}_{0.8}\text{Si}_{0.2}\text{O}_3$, $\text{SnPb}_{0.9}\text{Si}_{0.1}\text{O}_3$, $\text{SnPb}_{0.8}\text{Si}_{0.2}\text{O}_3$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{Pb}_{0.1}\text{O}_3$, $\text{SnP}_{0.9}\text{Ge}_{0.1}\text{O}_{3.45}$, $\text{SnP}_{0.8}\text{Ge}_{0.2}\text{O}_{3.4}$, $\text{SnP}_{0.5}\text{Ge}_{0.5}\text{O}_{3.25}$, $\text{SnP}_{0.9}\text{Pb}_{0.1}\text{O}_{3.45}$, $\text{SnP}_{0.8}\text{Pb}_{0.2}\text{O}_{3.4}$, $\text{SnP}_{0.5}\text{Pb}_{0.5}\text{O}_{3.25}$, $\text{SnGe}_{0.9}\text{P}_{0.1}\text{O}_{3.05}$, $\text{SnGe}_{0.8}\text{P}_{0.2}\text{O}_{3.1}$, $\text{SnPb}_{0.9}\text{P}_{0.1}\text{O}_{3.05}$, $\text{SnPb}_{0.8}\text{P}_{0.2}\text{O}_{3.1}$, $\text{SnP}_{0.8}\text{Ge}_{0.1}\text{Pb}_{0.1}\text{O}_{3.4}$, $\text{SnB}_{0.9}\text{Ge}_{0.1}\text{O}_{2.55}$, $\text{SnB}_{0.8}\text{Ge}_{0.2}\text{O}_{2.6}$, $\text{SnB}_{0.5}\text{Ge}_{0.5}\text{O}_{2.75}$, $\text{SnB}_{0.9}\text{Pb}_{0.1}\text{O}_{2.55}$, $\text{SnB}_{0.8}\text{Pb}_{0.2}\text{O}_{2.6}$, $\text{SnB}_{0.5}\text{Pb}_{0.5}\text{O}_{2.75}$, $\text{SnGe}_{0.9}\text{B}_{0.1}\text{O}_{2.95}$, $\text{SnGe}_{0.8}\text{B}_{0.2}\text{O}_{2.9}$, $\text{SnPb}_{0.9}\text{B}_{0.1}\text{O}_{2.95}$, $\text{SnPb}_{0.8}\text{B}_{0.2}\text{O}_{2.9}$, $\text{SnB}_{0.8}\text{Ge}_{0.1}\text{Pb}_{0.1}\text{O}_{2.6}$, $\text{SnSi}_{0.25}\text{B}_{0.2}\text{P}_{0.2}\text{O}_3$, $\text{SnSi}_{0.5}\text{B}_{0.2}\text{P}_{0.2}\text{O}_3$, $\text{SnSi}_{0.9}\text{Al}_{0.1}\text{O}_{2.95}$, $\text{SnSi}_{0.5}\text{Al}_{0.5}\text{O}_{2.75}$, $\text{SnSi}_{0.5}\text{Al}_{0.1}\text{O}_{2.15}$, $\text{SnSi}_{0.5}\text{Al}_{0.5}\text{O}_{2.75}$, $\text{SnSi}_{0.7}\text{Al}_{0.3}\text{O}_{2.85}$, $\text{SnSiAl}_{0.2}\text{O}_{3.3}$, $\text{SnSi}_{0.5}\text{B}_{0.05}\text{O}_{2.75}$, $\text{SnSi}_{0.5}\text{B}_{0.1}\text{O}_{2.15}$, $\text{SnSi}_{0.5}\text{B}_{0.5}\text{O}_{2.75}$, $\text{SnSi}_{0.7}\text{B}_{0.3}\text{O}_{2.45}$, $\text{SnSi}_{0.9}\text{B}_{0.1}\text{O}_{2.95}$, $\text{SnSiB}_{0.2}\text{O}_{3.3}$, $\text{SnSi}_{0.5}\text{Pb}_{0.05}\text{O}_{2.75}$, $\text{SnSi}_{0.5}\text{Pb}_{0.1}\text{O}_{2.15}$, $\text{SnSi}_{0.5}\text{Pb}_{0.5}\text{O}_{2.75}$, $\text{SnSi}_{0.7}\text{Pb}_{0.3}\text{O}_{2.45}$, $\text{SnSi}_{0.9}\text{Pb}_{0.1}\text{O}_{2.95}$, $\text{SnSiPb}_{0.2}\text{O}_{3.3}$, $\text{SnSi}_{0.1}\text{Ge}_{0.1}\text{P}_{0.9}\text{O}_{3.65}$, $\text{SnSi}_{0.2}\text{Ge}_{0.1}\text{P}_{0.7}\text{O}_{3.35}$, $\text{SnSi}_{0.6}\text{Ge}_{0.4}\text{P}_{0.1}\text{O}_{3.25}$, $\text{SnSi}_{0.6}\text{Ge}_{0.2}\text{P}_{0.2}\text{O}_{3.1}$, $\text{SnSi}_{0.7}\text{Ge}_{0.1}\text{P}_{0.2}\text{O}_{3.1}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{P}_{0.1}\text{O}_{3.05}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{P}_{0.3}\text{O}_{3.55}$, $\text{SnSiGe}_{0.1}\text{P}_{0.1}\text{O}_{3.45}$, $\text{SnSiGe}_{0.2}\text{P}_{0.2}\text{O}_{3.9}$, $\text{SnSiGe}_{0.1}\text{P}_{0.2}\text{O}_{3.7}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{Al}_{0.1}\text{O}_{2.95}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{B}_{0.1}\text{O}_{2.95}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{Sb}_{0.1}\text{O}_{2.95}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{In}_{0.1}\text{O}_{2.95}$, $\text{SnSi}_{0.8}\text{Ge}_{0.1}\text{Pb}_{0.1}\text{O}_{2.95}$, $\text{SnSi}_{0.8}\text{B}_{0.1}\text{Al}_{0.1}\text{O}_{2.9}$, $\text{SnSi}_{0.8}\text{Sb}_{0.1}\text{AlO}_{2.9}$, $\text{SnPAl}_{0.1}\text{O}_{3.65}$, $\text{SnPAl}_{0.3}\text{O}_{3.95}$, $\text{SnP}_{0.8}\text{Al}_{0.1}\text{O}_{3.15}$, $\text{SnP}_{0.8}\text{Al}_{0.3}\text{O}_{2.45}$, $\text{SnP}_{0.5}\text{Al}_{0.1}\text{O}_{2.4}$, $\text{SnP}_{0.5}\text{Al}_{0.3}\text{O}_{2.7}$, $\text{PbSi}_{0.01}\text{O}_{1.02}$, $\text{PbGe}_{0.01}\text{O}_{1.02}$, $\text{PbSi}_{0.01}\text{O}_{2.02}$, $\text{PbGe}_{0.01}\text{O}_{2.02}$, $\text{PbP}_{0.01}\text{O}_{1.025}$, $\text{PbB}_{0.01}\text{O}_{1.015}$, $\text{PbP}_{0.01}\text{O}_{2.025}$, $\text{PbGe}_{0.01}\text{O}_{2.015}$, $\text{PbSi}_{0.05}\text{O}_{1.1}$, $\text{PbGe}_{0.05}\text{O}_{1.1}$, $\text{PbSi}_{0.05}\text{O}_{2.1}$, $\text{PbGe}_{0.05}\text{O}_{2.1}$, $\text{PbP}_{0.05}\text{O}_{1.125}$, $\text{PbB}_{0.05}\text{O}_{1.075}$, $\text{PbP}_{0.05}\text{O}_{2.125}$, $\text{PbB}_{0.05}\text{O}_{2.075}$, $\text{PbSi}_{0.1}\text{O}_{2.2}$, $\text{PbGe}_{0.1}\text{O}_{2.2}$, $\text{PbSi}_{0.1}\text{O}_{1.2}$, $\text{PbGe}_{0.1}\text{O}_{1.2}$, $\text{PbP}_{0.1}\text{O}_{2.25}$, $\text{PbB}_{0.1}\text{O}_{2.15}$, $\text{PbP}_{0.1}\text{O}_{1.25}$, $\text{PbB}_{0.1}\text{O}_{1.15}$, $\text{PbSi}_{0.2}\text{O}_{2.4}$, $\text{PbGe}_{0.2}\text{O}_{2.4}$, $\text{PbSi}_{0.2}\text{O}_{1.4}$, $\text{PbGe}_{0.2}\text{O}_{1.4}$, $\text{PbP}_{0.2}\text{O}_{2.5}$, $\text{PbB}_{0.2}\text{O}_{2.3}$, $\text{PbP}_{0.2}\text{O}_{1.5}$, $\text{PbB}_{0.2}\text{O}_{1.3}$.

PbSi_{0.3}O_{2.6}, PbGe_{0.3}O_{2.6}, PbSi_{0.3}O_{1.6}, PbGe_{0.3}O_{1.6}, PbP_{0.3}O_{2.75}, PbB_{0.3}O_{2.45}, PbP_{0.3}O_{1.75}, PbB_{0.3}O_{1.45}, PbSi_{0.2}Ge_{0.1}O_{2.6}, PbGe_{0.2}Si_{0.1}O_{2.6}, PbP_{0.2}Ge_{0.1}O_{2.7}, PbGe_{0.2}P_{0.1}O_{2.65}, PbB_{0.2}Ge_{0.1}O_{2.5}, PbGe_{0.2}B_{0.1}O_{2.55}, PbSi_{0.7}O_{2.4}, PbGe_{0.7}O_{2.4}, PbP_{0.7}O_{2.75}, PbB_{0.7}O_{2.05}, PbSi_{0.8}O_{2.6}, PbGe_{0.8}O_{2.6}, PbP_{0.8}O₃, PbB_{0.8}O_{2.2}, PbSiO₃, PbGeO₃, PbPO_{3.5}, PbBO_{2.5}, PbSi_{0.9}Ge_{0.1}O₃, PbSi_{0.8}Ge_{0.2}O₃, PbSi_{0.5}Ge_{0.5}O₃,
 5 PbP_{0.9}Ge_{0.1}O_{3.45}, PbP_{0.8}Ge_{0.2}O_{3.4}, PbP_{0.5}Ge_{0.5}O_{3.25}, PbB_{0.9}Ge_{0.1}O_{2.65}, PbB_{0.8}Ge_{0.2}O_{2.6}, PbB_{0.5}Ge_{0.5}O_{2.75}, PbGe_{0.9}Si_{0.1}O₃, PbGe_{0.8}Si_{0.2}O₃, PbGe_{0.9}P_{0.1}O_{3.05}, PbGe_{0.8}P_{0.2}O_{3.1}, PbGe_{0.9}B_{0.1}O_{2.95}, PbGe_{0.8}B_{0.2}O_{2.9}, PbSi_{1.5}O₄, PbGe_{1.5}O₄, PbP_{1.5}O_{4.75}, PbB_{1.5}O_{3.25}, PbGe₂O₅, PbSi₂O₆, PbGe₂O₆, PbP₂O₇, PbB₂O₅, GeSi_{0.01}O_{1.02}, GeSi_{0.01}O_{2.02}, GeSi_{0.05}O_{1.1}, GeSi_{0.05}O_{2.1}, GeSi_{0.1}O_{1.2}, GeSi_{0.1}O_{2.2}, GeSi_{0.2}O_{1.4}, GeSi_{0.2}O_{2.4}, GeSi_{0.3}O_{1.6}, GeSi_{0.3}O_{2.6}, GeSi_{0.5}O₂, GeSi_{0.5}O₃, GeSi_{0.7}O_{2.4}, GeSi_{0.7}O_{3.4}, GeSiO₃, GeSiO₄, GeSi_{1.5}O₄,
 10 GeSi_{1.5}O₅, GeP_{0.01}O_{1.025}, GeP_{0.01}O_{2.025}, GeP_{0.05}O_{1.125}, GeP_{0.05}O_{2.125}, GeP_{0.1}O_{1.25}, GeP_{0.1}O_{2.25}, GeP_{0.2}O_{1.5}, GeP_{0.2}O_{2.5}, GeP_{0.3}O_{1.75}, GeP_{0.3}O_{2.75}, GeP_{0.5}O_{2.25}, GeP_{0.5}O_{3.25}, GeP_{0.7}O_{2.75}, GeP_{0.7}O_{3.75}, GePO_{3.5}, GePO_{4.5}, GeP_{1.5}O_{4.75}, GeP_{1.5}O_{5.75}, GeB_{0.01}O_{1.015}, GeB_{0.01}O_{2.015}, GeB_{0.05}O_{1.075}, GeB_{0.05}O_{2.075}, GeB_{0.1}O_{1.15}, GeB_{0.1}O_{2.15}, GeB_{0.2}O_{1.3}, GeB_{0.2}O_{2.3}, GeB_{0.3}O_{1.45}, GeB_{0.3}O_{2.45}, GeB_{0.5}O_{1.75}, GeB_{0.5}O_{2.75}, GeB_{0.7}O_{2.05}, GeB_{0.7}O_{3.05}, GeBO_{2.5}, GeBO_{3.5}, GeB_{1.5}O_{3.25} and GeB_{1.5}O_{4.25}.

15 The use of any of the compounds represented by formulae (I) to (V) as a main negative electrode active material affords a nonaqueous secondary battery having excellent charge and discharge cycle characteristics, a high discharge potential, a high capacity and high safety.

The pronouncedly excellent effects of the present invention come from the use of a compound containing Sn in which Sn is present with divalency. The valency of Sn can be determined through
 20 chemical titration, for example, according to the method described in *Physics and Chemistry of Glasses*, Vol. 8, No. 4, p. 165 (1967). It is also decided from the Knight shift in the solid nuclear magnetic resonance spectrum of Sn. For example, in broad-line NMR measurement, metallic Sn (zero valent Sn) shows a peak in an extremely low magnetic field in the vicinity of 7000 ppm with reference to Sn(CH₃)₄, whereas the peak of SnO (divalent Sn) appears around 100 ppm, and that of SnO₂ (tetravalent Sn) appears around -600 ppm.
 25 Like this, the Knight shift largely depends on the valency of Sn, the center metal, with the ligands being the same. The valency can thus be determined by the peak position obtained by ¹¹⁹Sn-NMR analysis.

The negative electrode active material of the present invention may contain various compounds, such as compounds of the group IA elements (e.g., Li, Na, K, Rb, and Cs), transition metals (e.g., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, lanthanoid metals, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg), the group IIA elements (e.g., Be, Mg, Ca, Sr, Ba), and the group VIIB elements (e.g., F, Cl, Br, I).
 30 Further, it may also contain dopants of various compounds (e.g., compounds of Sb, In, Nb) for improving electrical conductivity. The addition amount thereof is preferably 0 to 20 mol%.

The compounds of formulae (I) to (V) can be synthesized by either a calcination method or a solution method.

35 For instance, the calcination method is conducted by calcining a mixed compound of M¹ compound and M² compound (where M¹ and M², which are different from each other, each represent Si, Ge, Sn, Pb, P, B, Al, As, Sb).

The tin compounds include SnO, SnO₂, Sn₂O₃, Sn₃O₄, Sn₇O₁₃·H₂O, Sn₈O₁₅, stannous hydroxide, stannic oxyhydroxide, stannic acid, stannous oxalate, stannous phosphate, orthostannic acid, metastannic
 40 acid, parastannic acid, stannous fluoride, stannic fluoride, stannous chloride, stannic chloride, stannous bromide, stannic bromide, stannous iodide, stannic iodide, tin selenide, tin telluride, stannous pyrophosphate, tin phosphite, stannous sulfate, stannic sulfate.

The silicon compounds include SiO₂, SiO, organic silicon halide compounds such as silicon tetrachloride, silicon, tetrafluoride, trichloromethylsilane, dimethyldichlorosilane and tetraethylsilane, alkoxy
 45 compounds such as tetramethoxysilane and tetraethoxysilane, and hydroxysilane compounds such as trichlorohydroxysilane.

The germanium compounds include GeO₂, GeO, germanium tetrachloride, and alkoxy germanium compounds such as germanium tetramethoxide and germanium tetraethoxide.

The lead compounds include PbO₂, PbO, Pb₂O₃, Pb₃O₄, PbCl₂, lead chlorate, lead perchlorate, lead
 50 nitrate, lead carbonate, lead formate, lead acetate, lead tetraacetate, lead tartrate, lead diethoxide, lead di(isopropoxide).

The phosphorus compound includes phosphorus pentoxide, phosphorus oxychloride, phosphorous pentachloride, phosphorus trichloride, phosphorous tribromide, trimethyl phosphate, triethyl phosphate, tripropyl phosphate, stannous pyrophosphate, and boron phosphate.

55 The boron compound includes boron sesquioxide, boron trichloride, boron tribromide, boron carbide, boric acid, trimethyl borate, triethyl borate, tripropyl borate, tributyl borate, boron phosphide, and boron phosphate.

The aluminum compound includes aluminum oxide (α -alumina or β -alumina), aluminum silicate, aluminum triisopropoxide, aluminum tellurite, aluminum chloride, aluminum boride, aluminum phosphide, aluminum phosphate, aluminum lactate, aluminum borate, aluminum sulfide, and aluminum sulfate.

The antimony compound includes antimony tribromide, antimony trichloride, diantimony trioxide, and triphenylantimony.

Calcination is carried out preferably at a rate of temperature rise of 4° to $2000^{\circ}\text{C}/\text{min}$, still preferably 6° to $2000^{\circ}\text{C}/\text{min}$, most preferably 10° to $2000^{\circ}\text{C}/\text{min}$; at a calcination temperature of 250° to 1500°C , still preferably 350° to 1500°C , most preferably 500° to 1500°C ; for a period of 0.01 to 100 hours, still preferably 0.5 to 70 hours, most preferably 1 to 20 hours. After calcination, the system is cooled at a rate of temperature drop of 2° to $10^7^{\circ}\text{C}/\text{min}$, still preferably 4° to $10^7^{\circ}\text{C}/\text{min}$, still more preferably 6° to $10^7^{\circ}\text{C}/\text{min}$, most preferably 10° to $10^7^{\circ}\text{C}/\text{min}$.

The term "rate of temperature rise" as used herein means an average rate of temperature rise from 50% calcination temperature ($^{\circ}\text{C}$) up to 80% calcination temperature ($^{\circ}\text{C}$), and the term "rate of temperature drop" as used herein means an average rate of temperature drop from 80% calcination temperature ($^{\circ}\text{C}$) to 50% calcination temperature ($^{\circ}\text{C}$).

Cooling of the calcined product may be effected either within a calcining furnace or out of the furnace, for example, by pouring the product into water. Super-quenching methods described in Ceramics Processing, p. 217, Gihodo (1987), such as a gun method, a Hammer-Anvil method, a slap method, a gas atomizing method, a plasma spray method, a centrifugal quenching method, and a melt drag method, can also be used. Further, cooling may be conducted by a single roller method or a twin-roller method described in New Glass Handbook, p. 172, Maruzen (1991). Where the material melts during calcination, the calcined product may be withdrawn continuously while feeding the raw materials. The molten liquid is preferably stirred during calcination.

The calcining atmosphere preferably has an oxygen content of not more than 100% by volume, preferably not more than 20% by volume, more preferably not more than 5% by volume. An inert gas atmosphere is still preferred. Inert gas includes nitrogen, argon, helium, krypton, and xenon.

The compound of formulae (I) to (V) preferably has an average particle size of from 0.1 to $60\text{ }\mu\text{m}$. The calcined product can be ground to size by means of well-known grinding machines or classifiers, such as a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planetary ball mill, a spinning air flow type jet mill, and a sieve. If necessary, wet grinding using water or an organic solvent, such as methanol, may be conducted. The grinds are preferably classified to obtain a desired particle size either by dry or wet classification by means of a sieve, an air classifier, etc.

According to one of the embodiments of the present invention in which the negative electrode active material is an oxide containing fluorine, the fluorine in the negative electrode active material strengthens the structure and chemical stability of a compound oxide. In particular, fluorine in an amorphous oxide is effective to further enhance the amorphous properties thereby improving the electrochemical structural stability.

Specific examples of the fluorine-containing negative electrode active material or a precursor thereof are $\text{GeF}_{0.2}\text{O}_{0.9}$, $\text{GeF}_{0.2}\text{O}_{1.9}$, $\text{SnF}_{0.2}\text{O}_{0.9}$, $\text{SnF}_{0.2}\text{O}_{1.9}$, $\text{SnSiF}_{0.4}\text{O}_{2.8}$, $\text{PbF}_{0.4}\text{O}_{1.8}$, $\text{PbF}_{0.2}\text{O}_{1.9}$, $\text{Pb}_2\text{F}_{0.2}\text{O}_{2.9}$, $\text{Pb}_3\text{F}_{0.4}\text{O}_{3.8}$, $\text{Sb}_2\text{F}_{0.2}\text{O}_{2.9}$, $\text{Sb}_2\text{F}_{0.2}\text{O}_{3.9}$, $\text{Sb}_2\text{F}_{0.2}\text{O}_{4.9}$, $\text{Bi}_2\text{F}_{0.4}\text{O}_{3.8}$, and $\text{Bi}_2\text{F}_{0.2}\text{O}_{4.9}$, and non-stoichiometrical compounds or compound oxides thereof.

Preferred of these fluorine-containing negative electrode active materials are fluorine-containing SnO , SnO_2 , GeO , GeO_2 , and SnSiO_3 , with fluorine-containing SnSiO_3 being still preferred. Fluorine-containing and amorphous SnO , SnO_2 , GeO , GeO_2 , and SnSiO_3 are particularly preferred.

A preferred fluorine content in the fluorine-containing negative electrode active material is from 10 to 100 mol%, particularly 20 to 50 mol%, based on the total amount of the metal elements in the active material.

The F-containing negative electrode active materials preferably include those represented by formula $\text{Sn}_x\text{SiF}_y\text{O}_z$ ($0.2 < x \leq 1.0$; $0 < y \leq 2$; $2.2 < z \leq 3$). The F-containing compound oxide may be crystalline or amorphous but is preferably amorphous.

The F-containing negative electrode active material precursor mainly comprising Sn can be synthesized by calcining a mixture of the above-mentioned tin oxide and fluorine compound in air or an inert gas at a high temperature.

In the case of adding another metal or metals, a mixture of the tin compound, the fluorine compound, and an oxide of another metal or metals is calcined. For example, fluorine-containing SnSiO_3 can be synthesized by calcining a mixture of SnO , SnF_2 , and SiO_2 in an inert gas at 200° to 1200°C , preferably 500° to 1100°C .

For obtaining an amorphous (glassy) active material, the calcined product is quenched at a cooling rate of 1.5° to 100° C/min, preferably 5° to 20° C/min.

The fluorine-containing negative electrode active material precursor can also be synthesized by co-precipitation in a solution (co-precipitation method). In this case, an acidic or alkaline aqueous solution containing, for example a salt of the group IIIB, IVB, or VB element is neutralized in the presence of a fluoride ion to form a fluorine-containing compound hydroxide or a fluorine-containing compound oxide.

The negative electrode active material precursors containing other metals can also be synthesized by the above-described calcination method or co-precipitation method.

The positive electrode active material which can be used in the present invention may be a transition metal oxide capable of reversibly intercalating and deintercalating a lithium ion but is preferably a lithium-containing transition metal oxide.

Lithium-containing transition metal oxides which can be used as a positive electrode active material include, for preference, lithium-containing oxides of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo or W. The oxide may contain other alkali metals (the group IA and IIA elements) in addition to Li and/or other elements such as Al, Ga, In, Ge, Sn, Pb, Sb, Bi, Si, P, B, etc. The ratio of these additional elements is preferably up to 30 mol%, still preferably up to 10 mol%, based on the transition metal.

Preferred of the Li-containing transition metal oxides as a positive electrode active material are those prepared from a mixture of a lithium compound and at least one compound of a transition metal selected from Ti, V, Cr, Mn, Fe, Co, Ni, Mo, and W at a lithium compound/total transition metal compounds molar ratio of 0.3 to 2.2.

Still preferred are those prepared from a mixture of a lithium compound and at least one compound of a transition metal selected from V, Cr, Mn, Fe, Co, and Ni at a lithium compound/total transition metal compounds molar ratio of from 0.3 to 2.2.

The most preferred are those represented by formula Li_xQO_y (Q represents at least one transition metal selected from Co, Mn, Ni, V, and Fe; x is from 0.2 to 1.2; and y is from 1.4 to 3). Q may contain, in addition to a transition metal, other metals, such as Al, Ga, In, Ge, Sn, Pb, Sb, Bi, Si, P, B, etc. The ratio of the other metals is preferably up to 30 mol% based on the total transition metals.

Suitable examples of the lithium-containing metal oxide positive electrode active material which can be preferably used in the present invention are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{Fe}_{1-b}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Co}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Ni}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{V}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Fe}_{2-c}\text{O}_4$, a mixture of $\text{Li}_x\text{Mn}_2\text{O}_4$ and MnO_2 , a mixture of $\text{Li}_{2x}\text{MnO}_3$ and MnO_2 , a mixture of $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_{2x}\text{MnO}_3$, and MnO_2 - (wherein x = 0.2 to 1.2; a = 0.1 to 0.9; b = 0.8 to 0.98; c = 1.6 to 1.96; and z = 2.01 to 5).

Preferred examples of the lithium-containing metal oxide positive electrode active materials are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{Fe}_{1-b}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Co}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Ni}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{V}_{2-c}\text{O}_4$, and $\text{Li}_x\text{Mn}_c\text{Fe}_{2-c}\text{O}_4$ (wherein x = 0.7 to 1.2; a = 0.1 to 0.9; b = 0.8 to 0.98; c = 1.6 to 1.96; z = 2.01 to 2.3).

Still preferred of the lithium-containing metal oxide positive electrode active materials are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, and $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ (wherein x = 0.7 to 1.2; a = 0.1 to 0.9; b = 0.9 to 0.98; and z = 2.01 to 2.3).

The most preferred are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, and $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ - (wherein x = 0.7 to 1.2; a = 0.1 to 0.9; b = 0.9 to 0.98; and z = 2.02 to 2.3).

The value x in the above formulae is the value before commencement of charging and discharging and varies with a charge and a discharge.

According to another embodiment of the present invention, a spinel type manganese-containing oxide is used as a positive electrode active material. Spinel type oxides have a spinel structure represented by formula $\text{A}(\text{B}_2)\text{O}_4$, in which the oxygen anions are aligned in cubic closest packing and occupy part of the faces and apexes of a tetrahedron and an octahedron. The unit cell is composed of 8 molecules, and oxygen occupies 32e positions in the Fd3m space. The unit cells occupy the lattice spacing of 64 octahedrons at three crystallographically non-equivalent positions, 8a, 8b, and 48f. In this spinel structure, cations B are positioned at the lattice spacing sites of the 16d octahedrons (the vacant octahedron site is 16c), and cations A are positioned at the lattice spacing sites of the 8a tetrahedrons. Each 8a octahedron shares the face with the adjoining 4 vacant 16c octahedrons thereby to provide passageways through which cations A diffuse (e.g., $8a \rightarrow 16c \rightarrow 8a \rightarrow 16c$). On the other hand, each 8b tetrahedron shares the face with the 16d octahedron formed of cations B, resulting in energy disadvantage to cations' occupation. The 48f tetrahedron shares the face with both the 16d and 16c octahedrons. According to the distribution of cations A, $\text{A}(\text{B}_2)\text{O}_4$ is called a normal spinel structure, and $\text{B}(\text{AB})\text{O}_4$ is called an inverse-spinel structure. $\text{A}_x\text{B}_y(\text{A}_{1-x}\text{B}_{1-y})\text{O}_4$, an intermediate structure between a normal spinel and an inverse-spinel, is also called a spinel.

Manganese oxides having a normal spinel structure typically include LiMn_2O_4 , which serves as a positive electrode active material. In this structure, a half of the Mn cations are trivalent, with the another half being tetravalent. $\lambda\text{-MnO}_2$, also known as an active material, is regarded to have a spinel structure with defects, derived by removing lithium from LiMn_2O_4 , in which all the Mn cations are tetravalent, as described in U.S. Patent 4,246,253. The manganese oxide positive electrode active materials which can be used in the present invention include all of those having a normal spinel structure, those having an inverse-spinel structure, those having a defect-free structure, and those having a non-stoichiometrical spinel structure with defects.

Suitable Li-containing manganese oxides having a spinel structure which can be used in the present invention include those represented by general formula $\text{Li}_{1+x}[\text{Mn}_{2-y}\text{O}_4]$ ($0 < x < 1.7$; $0 \leq y < 0.7$). Such compounds include $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (or $\text{Li}[\text{Li}_{1/3}\text{Mn}_{5/3}\text{O}_4]$). In addition, the following compounds are also included under the scope covered by the above general formula (structural formulae include those represented by multiplying the general formula by an integer or a decimal):

$\text{Li}_4\text{Mn}_4\text{O}_9$, LiMnO_2 (or $\text{Li}_2\text{Mn}_2\text{O}_4$), Li_2MnO_3 , $\text{Li}_5\text{Mn}_4\text{O}_9$, and $\text{Li}_4\text{Mn}_5\text{O}_{12}$

Suitable Li-containing manganese oxides having a spinel structure which can be used as a positive electrode active material in the present invention further include those represented by general formula $\text{Li}_{1-x}[\text{Mn}_{2-y}\text{O}_4]$ ($0 < x < 1.0$; $0 \leq y < 0.5$). Preferred of them are those represented by general formula $\text{Li}_{1-x}[\text{Mn}_{2-y}\text{O}_4]$ ($0.20 < x < 1.0$; $0 < y < 0.2$), such as $\text{Li}_2\text{Mn}_5\text{O}_{11}$ (or $\text{Li}_{1-x}[\text{Mn}_{2-y}\text{O}_4]$ ($x = 0.273$; $y = 0.182$)), which is a non-stoichiometrical spinel compound disclosed in JP-A-4-240117; and those represented by general formula $\text{Li}_{1-x}[\text{Mn}_{2-y}\text{O}_4]$ ($0 < x \leq 0.20$; $0 < y < 0.4$), such as $\text{Li}_2\text{Mn}_4\text{O}_9$. In addition, the following compounds are also included under the scope covered by the above formula $\text{Li}_{1-x}[\text{Mn}_{2-y}\text{O}_4]$ (structural formulae include those represented by multiplying the general formula by an integer or a decimal):

$\text{Li}_4\text{Mn}_{16.5}\text{O}_{35}$, $\text{Li}_2\text{Mn}_{7.5}\text{O}_{16}$, and $\text{Li}_{0.7}\text{MnO}_4$

The above-mentioned spinel type manganese oxides as a positive electrode active material can be obtained by reacting a lithium salt and a manganese salt or a manganese oxide in a solid phase at a high temperature according to a known method. In using lithium carbonate and manganese dioxide as starting materials, calcination is carried out at 350°C to 900°C , preferably 350°C to 500°C , for 8 to 48 hours. In using lithium nitrate having a low melting point (261°C) as a lithium salt, calcination is carried out at 300°C to 900°C , preferably 300°C to 500°C . Manganese oxides to be used include $\lambda\text{-MnO}_2$, electrolytically prepared MnO_2 (EMD), chemically prepared MnO_2 (CMD), and a mixture thereof. Lithium-manganese double oxides (e.g., $\text{Li}_2\text{Mn}_4\text{O}_9$) may also be used as a lithium material. In this case, the Li-Mn double oxide is mixed with a manganese material, e.g., manganese dioxide, and calcined at 350°C to 500°C .

The spinel type manganese oxide may be doped with one or more of other transition metal elements, typical elements, and rare earth elements to form a compound oxide. Preferred dopants are transition metal elements, such as Co, Ni, Ti, V, Zr, Nb, Mo, W, and Fe.

The positive electrode active materials which can be used in the present invention also include manganese oxide compounds having a hollandite skeleton structure as disclosed in JP-A-4-270125, which are regarded as having the above-described general formulae with part or most part (e.g., 95% or more) of Li cations thereof being substituted with other cations, e.g., H, K, Na, and ammonium ions. Hollandite type compounds in which Li cations are substituted with H can easily be obtained by, for example, treating an Li-Mg double oxide represented by the above general formula with an acid at a high temperature to remove Li.

The positive electrode active materials can be synthesized by mixing a lithium compound and a transition metal compound, followed by calcination or by reacting these materials in a solution. The former calcination method is preferred.

Calcination is carried out at a calcination temperature selected from the range in which at least part of the mixed compounds may be decomposed and melted, for example, from 250°C to 2000°C , preferably from 350°C to 1500°C , for 1 to 72 hours, preferably 2 to 20 hours. Prior to calcination, the mixture is preferably pre-calcined at 250°C to 900°C . Mixing of the raw materials may be either dry blending or wet blending. If desired, calcination may be followed by annealing at 200°C to 900°C .

The calcination atmosphere is not limited and may be an oxidizing atmosphere or a reducing atmosphere. For example, calcination can be performed in air, a prepared gas having an arbitrary oxygen concentration, hydrogen, carbon monoxide, nitrogen, argon, helium, krypton, xenon, or carbon dioxide.

In the synthesis of positive electrode active materials, chemical intercalation of a lithium ion into a transition metal oxide is preferably achieved by reacting metallic lithium, a lithium alloy or butyl lithium with

the transition metal oxide.

While not limiting, the positive electrode active material to be used in the present invention preferably has an average particle size of from 0.1 to 50 μm and a BET specific surface area of from 0.01 to 50 m^2/g . An aqueous solution (supernatant liquid) of 5 g of a positive electrode active material in 100 ml of distilled water preferably has a pH of 7 to 12.

The resulting positive electrode active material can be ground to size by means of well-known grinding machines or classifiers, such as a mortar, a ball mill, a vibration ball mill, a vibration mill, a satellite ball mill, a planetary ball mill, a spinning air flow type jet mill, and a sieve.

If desired, the positive electrode active material obtained by calcination may be washed with water, an aqueous acid solution, an aqueous alkali solution or an organic solvent before use.

A preferred combination of a negative electrode active material and a positive electrode active material is a combination of a compound of formula (I) as a negative electrode active material and Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, Li_xMnO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, or $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ ($x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.9$ to 0.98 ; and $z = 2.02$ to 2.3) as a positive electrode active material, still preferably a combination of a compound of formula (III) and Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, Li_xMnO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, or $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ ($x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.9$ to 0.98 ; and $z = 2.02$ to 2.3) as a positive electrode active material, most preferably a combination of a compound of formula (IV) as a negative electrode active material and Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, Li_xMnO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, or $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ ($x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.9$ to 0.98 ; and $z = 2.02$ to 2.3) as a positive electrode active material.

Further, preferred is a combination of a compound of formula (I) as a negative electrode active material and $\text{Li}_4\text{Mn}_4\text{O}_9$, LiMnO_2 , $\text{Li}_2\text{Mn}_2\text{O}_4$, Li_2MnO_3 , $\text{Li}_5\text{Mn}_4\text{O}_9$, $\text{Li}_4\text{Mn}_5\text{O}_{12}$, $\text{Li}_4\text{Mn}_{16.5}\text{O}_{35}$, $\text{Li}_2\text{Mn}_{7.5}\text{O}_{16}$ or $\text{Li}_{0.7}\text{Mn}_2\text{O}_4$.

Such combinations of active materials afford a nonaqueous secondary battery having excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

Lithium is intercalated into a compound represented by any of formulas (I) to (V) in an amount of from 1 to 20 equivalents, preferably from 3 to 10 equivalents.

The ratio of a positive electrode active material to a negative electrode active material is decided according to the above-mentioned equivalent amount. It is preferable to use a positive electrode active material in an amount based on the calculated ratio multiplied by 0.5 to 2. Where any other substance than a positive electrode active material, e.g., metallic lithium, a lithium alloy or butyl lithium, is used as a lithium source, the amount of a positive electrode active material to be used is decided in conformity with the equivalent amount of deintercalated lithium of the negative electrode active material. In this case, too, the ratio based on the equivalent amount is preferably multiplied by 0.5 to 2.

Negative electrode active materials which may be used in combination with the negative electrode active material of the present invention include metallic lithium, lithium alloys (e.g., alloys with Al, Al-Mn, Al-Mg, Al-Sn, Al-In or Al-Cd), and calcined carbonaceous compounds capable of intercalating and deintercalating a lithium ion or metallic lithium.

The purpose of the combined use of metallic lithium or a lithium alloy is to intercalate lithium into a compound mainly comprising an oxide of formula (I) to (V) within a cell but not to utilize the dissolution-precipitation reaction of metallic lithium, etc. as an electrode reaction.

An electrode material mixture which can be used in the present invention comprises the above-described active material, a conducting agent, a binder, a filler, and so forth.

The conducting agent may be any electron-conducting material which undergoes no chemical change in an assembled battery. Suitable conducting agents include natural graphite (scale graphite, flake graphite, lumpy graphite, etc.), artificial graphite, carbon black, acetylene black, Ketjen black, carbon fiber, metal powders (e.g., copper, nickel, aluminum or silver powder), metallic fibers, polyphenylene derivatives, and mixtures of two or more thereof. A combination of graphite and acetylene black is particularly preferred.

The conducting agent is preferably used in an amount of from 1 to 50% by weight, still preferably from 2 to 30% by weight, based on the total weight of the active material mixture. Carbon or graphite is preferably used in an amount of from 2 to 15% by weight.

The binder includes polysaccharides, thermoplastic resins, and rubbery polymers; such as starch, polyvinyl alcohol, carboxymethyl cellulose, hydroxypropyl cellulose, regenerated cellulose, diacetyl cellulose, polyvinyl chloride, polyvinyl pyrrolidone, tetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, ethylene-propylene-diene terpolymers (EPDM), sulfonated EPDM, styrene-butadiene rubbers, polybutadiene, fluorine rubbers, polyethylene oxide, and mixtures of two or more thereof. In using a compound having a functional group reactive with lithium, such as a polysaccharide, it is preferable to deactivate the functional group by addition of a compound having an isocyanate group. The binder is used in an amount of 1 to 50% by weight, preferably 2 to 30% by weight, based on the total weight of the active

material mixture.

In particular, polymers having a decomposition temperature of not lower than 300 °C are preferred as a binder for the negative electrode active material of the present invention. Such polymers include polyethylene, polypropylene, epoxy resins, polyester resins, and fluorine resins, with fluorine resins being preferred.

5 The term "fluorine resin" is used herein as a general term for polymers having a carbon-fluorine bond in the molecule thereof as specified in JIS K6900 "Glossary of Terms Used in Plastic Industry".

Suitable examples of the fluorine resins are shown below.

- (A-1) Polytetrafluoroethylene (PTFE)
- (A-2) Polyvinylidene fluoride (PVDF)
- 10 (A-3) Tetrafluoroethylene-hexafluoropropylene copolymer (FEP)
- (A-4) Tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA)
- (A-5) Vinylidene fluoride-hexafluoropropylene copolymer
- (A-6) Vinylidene fluoride-chlorotrifluoroethylene copolymer
- (A-7) Ethylene-tetrafluoroethylene copolymer (ETFE resin)
- 15 (A-8) Polychlorotrifluoroethylene (PCTFE)
- (A-9) Vinylidene fluoride-pentafluoropropylene copolymer
- (A-10) Propylene-tetrafluoroethylene copolymer
- (A-11) Ethylene-chlorotrifluoroethylene copolymer (ECTFE)
- (A-12) Vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene copolymer
- 20 (A-13) Vinylidene fluoride-perfluoromethyl vinyl ether-tetrafluoroethylenecopolymer

Copolymer resins comprising another ethylenically unsaturated monomer in addition to the above-mentioned monomers are also useful. Specific but non-limiting examples of copolymerizable unsaturated monomers include acrylic esters, methacrylic esters, vinyl acetate, acrylonitrile, acrylic acid, methacrylic acid, maleic anhydride, butadiene, styrene, N-vinylpyrrolidone, N-vinylpyridine, glycidyl methacrylate, 25 hydroxyethyl methacrylate, and methyl vinyl ether.

The binder resins can be obtained by any of solution polymerization, emulsion polymerization, suspension polymerization, and gaseous phase polymerization, and the polymer may be any of random polymers, graft polymers, and block polymers.

The above-mentioned binder resin may be used in combination with one or more other polymers, such as 30 carboxymethyl cellulose, sodium polyacrylate, hydroxyethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxide, and alginic acid.

The binder is preferably used in an amount of from 0.5 to 30% by weight based on the negative electrode active material.

The filler to be used in the present invention is not particularly limited as long as it is a fibrous material 35 undergoing no chemical change in an assembled battery. Suitable fillers include fibers of polyolefins (e.g., polypropylene or polyethylene), glass fiber, and carbon fiber. While not limiting, the filler is preferably used in an amount of up to 30% by weight based on the total weight of the active material mixture.

The nonaqueous electrolytic solution which can be used in the nonaqueous secondary battery of the present invention consists of at least one organic solvent and at least one lithium salt soluble in the solvent. 40 Suitable organic solvents include aprotic solvents, such as propylene carbonate, ethylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, γ -butyrolactone, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolane, formamide, dimethylformamide, dioxolane, acetonitrile, nitromethane, methyl formate, methyl acetate, methyl propionate, ethyl propionate, phosphoric triesters, trimethoxymethane, dioxolane derivatives, sulfolane, 3-methyl-2-oxazolidinone, propylene carbonate derivatives, tetrahydrofuran derivatives, ethyl ether, and 1,3-propanesultone. These solvents may be used either individually or in combination of two or more thereof. Suitable lithium salts soluble in these solvents include LiClO_4 , LiBF_6 , LiPF_6 , LiCF_3SO_3 , LiCF_3CO_2 , LiAsF_6 , LiSbF_6 , $\text{LiB}_{10}\text{Cl}_{10}$, lower aliphatic lithium carboxylates, LiAlCl_4 , LiCl , LiBr , LiI , chloroborane lithium, and lithium tetraphenylborate. These lithium salts may be used either individually or in combination of two or more thereof. In 50 particular, a solution of LiCF_3SO_3 , LiClO_4 , LiBF_4 and/or LiPF_6 in a mixed solvent of propylene carbonate or ethylene carbonate and 1,2-dimethoxyethane and/or diethyl carbonate is a preferred electrolytic solution.

The amount of the electrolytic solution to be used in a battery is not particularly limited and can be selected according to the amounts of the positive and negative electrode active materials or the size of the battery.

55 The concentration of the supporting electrolyte is preferably from 0.2 to 3 mols per liter of the electrolytic solution.

In addition to electrolytic solutions, inorganic or organic solid electrolytes may also be employed.

Examples of suitable inorganic solid electrolytes include a lithium nitride, a lithium halide, and a lithium oxyacid salt. Among them preferred are Li_3N , LiI , Li_5Nl_2 , $\text{Li}_3\text{N-LiI-LiOH}$, LiSiO_4 , $\text{LiSiO}_4\text{-LiI-LiOH}$, $x\text{Li}_3\text{PO}_4\text{-(1-x)Li}_4\text{SiO}_4$, Li_2SiS_3 , and phosphorus sulfide compounds.

Examples of suitable organic solid electrolytes include polyethylene oxide derivatives or polymers containing the same (see JP-A-63-135447), polypropylene oxide derivatives or polymers containing the same, polymers containing an ionizing group (see JP-A-62-254302, JP-A-62-254303, and JP-A-63-193954), a mixture of a polymer containing an ionizing group and the above-mentioned aprotic electrolytic solution (see U.S. Patents 4,792,504 and 4,830,939, JP-A-62-22375, JP-A-62-22376, JP-A-63-22375, JP-A-63-22776, and JP-A-1-95117), and phosphoric ester polymers (see JP-A-61-256573). A combination of polyacrylonitrile and an electrolytic solution (see JP-A-62-278774) and a combination of an organic solid electrolyte and an inorganic solid electrolyte (see JP-A-60-1768) are also known.

As a separator, an insulating thin film having high ion permeability and prescribed mechanical strength is used. A sheet or nonwoven fabric made of an olefin polymer (e.g., polypropylene), glass fiber or polyethylene is usually employed for their organic solvent resistance and hydrophobic properties. The pore size of the separator is selected from the range generally used for batteries, e.g., from 0.01 to 10 μm . The thickness of the separator is selected from the range generally used for batteries, e.g., from 5 to 300 μm .

For the purpose of improving charge and discharge characteristics, the electrolytic solution may contain other compounds, such as pyridine (see JP-A-49-108525), triethyl phosphite (see JP-A-47-4376), triethanolamine (see JP-A-52-72425), a cyclic ether (see JP-A-57-152684), ethylenediamine (see JP-A-58-87777), n-glyme (see JP-A-58-87778), hexaphosphoric acid triamide (see JP-A-58-87779), a nitrobenzene derivative (see JP-A-58-214281), sulfur (see JP-A-59-8280), a quinoneimine dye (see JP-A-59-68184), an N-substituted oxazolidinone and an N,N'-substituted imidazolidinone (see JP-A-59-154778), an ethylene glycol dialkyl ether (see JP-A-59-205167), a quaternary ammonium salt (see JP-A-60-30065), polyethylene glycol (see JP-A-60-41773), pyrrole (see JP-A-60-79677), 2-methoxyethanol (see JP-A-60-89075), AlCl_3 (see JP-A-61-88466), a monomer providing a conductive polymeric active material (see JP-A-61-161673), triethylenephosphoramidate (see JP-A-61-208758), a trialkylphosphine (JP-A-62-80976), morpholine (see JP-A-62-80977), an aryl compound having a carbonyl group (see JP-A-62-86673), hexamethylphosphoric triamide and a 4-alkylmorpholine (see JP-A-62-217575), a bicyclic tertiary amine (see JP-A-62-217578), an oil (see JP-A-62-287580), a quaternary phosphonium salt (see JP-A-63-121268), and a tertiary sulfonium salt (see JP-A-63-121269).

In order to make the electrolytic solution incombustible, a halogen-containing solvent, such as carbon tetrachloride or trifluorochloroethylene, may be added to the electrolytic solution (see JP-A-48-36632). In order to make the electrolytic solution resistant to high-temperature preservation, carbonic acid gas may be incorporated thereto (see JP-A-59-134567).

The positive or negative electrode active material mixture may contain an electrolytic solution or an electrolyte. For example, it is known to add the above-mentioned ion-conductive polymer or nitromethane (see JP-A-48-36633) or an electrolytic solution (see JP-A-57-12487) to the active material mixture.

The surface of the positive electrode active material may be modified by treating with an esterification agent (see JP-A-55-163779), a chelating agent (see JP-A-55-163780), a conducting high polymer (see JP-A-58-163188 and JP-A-59-14274), polyethylene oxide (see JP-A-60-97561), and the like.

The surface of the negative electrode active material may also be modified by, for example, providing a layer comprising an ion-conductive polymer or polyacetylene (see JP-A-58-111276) or treating with LiCl (see JP-A-58-142771).

A collector for an active material may be made of any electron-conducting substance which undergoes no chemical change in an assembled battery. Suitable materials of a collector for the positive electrode include stainless steel, nickel, aluminum, titanium, calcined carbon; and aluminum or stainless steel with its surface treated with carbon, nickel, titanium or silver. Suitable materials of a collector for the negative electrode include stainless steel, nickel, copper, titanium, aluminum, calcined carbon; copper or stainless steel with its surface treated with carbon, nickel, titanium or silver; and an Al-Cd alloy. These materials may be subjected to surface oxidation. The collector may have a variety of forms, such as a foil, a film, a sheet, a net, a punched sheet, a lath, a porous body, a foamed body, a fibrous body, and so on. While not limiting, the thickness of the collector is from 1 to 500 μm .

The battery according to the present invention may have any shape, such as a coin shape, a button shape, a sheet shape, a cylindrical shape, and an angular shape.

A coin-shaped or button-shaped battery is generally produced by compressing a positive or negative active material mixture into a pellet having prescribed thickness and diameter according to the size of the battery. A sheet, cylindrical or angular battery is generally produced by coating a collector with a positive or negative active material mixture, followed by drying and compressing. The thickness, length or width of the

coating layer are decided according to the size of the battery. In particular, the dry thickness (thickness after compression) is preferably selected from the range 1 to 2000 μm .

The application of the nonaqueous secondary battery of the present invention is not particularly limited. For example, it is useful in electronic equipment, such as notebook-size color or monochromatic personal computers, pen input personal computers, pocket-size (palmtop) personal computers, notebook-size word processors, pocket-size word processors, electron book players, pocket phones, wireless extensions of key telephone sets, pagers, handy terminals, portable facsimiles, portable copying machines, portable printers, headphone stereos, video cameras, liquid crystal TV sets, handy cleaners, portable CD, mini disk systems, electrical shavers, machine translation systems, land mobile radiotelephones, transceivers, electrical tools, portable calculators, memory cards, tape recorders, radios, backup powers, and so on; automobiles, electrically-powered vehicles, motors, lights, toys, family (home) computers, load conditioners, irons, watches, stroboscopic lamps, cameras, medical equipment (e.g., pacemakers, hearing aids, and massaging machines); military equipment; and spacecraft equipment. The nonaqueous secondary battery of the present invention may be used in combination with solar batteries.

The present invention will now be illustrated in greater detail with reference to Examples, but the present invention should not be construed as being limited thereto. All the percents are by weight unless otherwise indicated.

SnO , GeO , GeO_2 , PbO , PbO_2 , Pb_2O_3 , Pb_3O_4 , Sb_2O_3 , Sb_2O_4 , Bi_2O_3 , LiCoO_2 , LiNiO_2 , LiMn_2O_4 used in Examples are commercially available ones.

Preparation of SnO_2 :

Sn(OH)_4 synthesized from SnCl_4 and NaOH was calcined in air at 400°C for 4 hours to obtain SnO_2 , and the resulting SnO_2 was ground in a mortar to an average primary particle size of about 0.05 μm (rutile structure).

Preparation of $\text{LiCo}_{0.95}\text{V}_{0.05}\text{O}_{2.07}$:

A mixture of Li_2CO_3 , CoCO_3 , and NH_4VO_3 was calcined at 900°C for 6 hours, followed by grinding in a mortar.

EXAMPLE A-1

In order to examine how close the negative electrode active material of the present invention is to metallic lithium, an average potential of lithium deintercalation with reference to Li-Al (80%-20%) and its capacity were measured.

A coin lithium battery having the structure shown in Fig. 2 was assembled in a dry box (dew point: -40° to -70°C ; dry air) using the following materials.

Electrode:

A negative electrode active material mixture consisting of 82% of each of the negative electrode active material precursors shown in Table A-1, 8% of flake graphite and 4% of acetylene black as conducting agents, and 6% of polyvinylidene fluoride as a binder was compression molded into a pellet of 13 mm in diameter and 22 mg in weight. Before use, the pellet was dried in the above-described dry box by means of a far infrared heater at 150°C for 3 hours.

Counter Electrode:

An Li-Al (80%-20%) pellet of 15 mm in diameter and 100 mg in weight.

Collector:

A 80 μm thick net of SUS316 was welded to each of a positive electrode case and a negative electrode case.

Electrolytic Solution:

200 μ l of a 1 mol/l solution of LiPF_6 in a 2:2:6 (by volume) mixed solvent of ethylene carbonate, butylene carbonate and dimethyl carbonate.

Separator:

A finely porous polypropylene sheet and polypropylene nonwoven fabric impregnated with the electrolytic solution.

The resulting lithium battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm², a cut-off voltage of 1.3 V in charging, and a cut-off voltage of 0.2 V in discharging. All the tests were started with intercalation of lithium into the compound of the present invention. The results obtained are shown in Table A-1.

Symbols used in Table A-1 and Tables A-2 to A-8 hereinafter given have the following meanings:

- (a) ... negative electrode active material precursor of the present invention
- (b) ... lithium deintercalation capacity in the first cycle (mAh/g-negative electrode active material precursor)
- (c) ... average potential (V) of lithium deintercalation
- (d) ... cycle characteristics [(lithium deintercalation capacity in the 10th cycle - lithium deintercalation capacity in the 1st cycle)/lithium deintercalation capacity in the 1st cycle]
- (e) ... discharge capacity in the 1st cycle (mAh/ml-cylindrical battery volume)

TABLE A-1

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d)
1	SnO	540	0.62	0.06
2	SnO ₂	499	0.67	0.05
3	GeO	358	0.65	0.02
4	GeO ₂	259	0.68	-0.29
5	PbO	309	0.58	0.55
6	PbO ₂	283	0.62	0.53
7	Pb ₂ O ₃	301	0.60	0.57
8	Pb ₃ O ₄	296	0.59	0.57
9	Sb ₂ O ₃	358	1.10	0.02
10	Sb ₂ O ₄	222	1.10	-0.18
11	Bi ₂ O ₃	345	0.88	0.63

EXAMPLE A-2

A coin battery was prepared in the same manner as in Example A-1, except for using the following counter electrode.

A positive electrode active material mixture consisting of 82% of LiCoO_2 , 8% of flake graphite, 4% of acetylene black, and 6% of tetrafluoroethylene was compression molded to obtain a pellet of 13 mm in diameter. The weight of the pellet was decided according to the lithium intercalation capacity of the negative electrode active material precursor. The charge capacity of LiCoO_2 was 170 mAh/g. Before assembly, the pellet was dried in the same manner as in Example A-1.

The resulting lithium battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm², a cut-off voltage of 4.3 V in charging, and a cut-off voltage of 2.7 V in discharging. All the tests were started with charging. The results obtained are shown in Table A-2.

TABLE A-2

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d)
1	SnO	485	3.52	0.08
2	SnO ₂	443	3.48	0.07
3	GeO	320	3.50	0.03
4	GeO ₂	229	3.46	-0.15
5	PbO	286	3.56	0.48
6	PbO ₂	261	3.52	0.55
7	Pb ₂ O ₃	275	3.50	0.49
8	Pb ₃ O ₄	279	3.54	0.49
9	Sb ₂ O ₃	320	3.04	0.04
10	Sb ₂ O ₄	195	3.05	-0.02
11	Bi ₂ O ₃	302	3.27	0.65

EXAMPLE A-3

In order to examine the influences of the calcination temperature in the synthesis of a negative electrode active material, the same test as in Run No. 2 of Example A-1 was conducted, except for varying the calcination temperature for the synthesis of SnO₂ as shown in Table A-3. The results obtained are shown in Table A-3.

TABLE A-3

Run No.	Calcination Temperature (°C)	(b) (mAh/g)	(c) (V)	(d)
1	300	499	0.68	0.05
2	500	515	0.68	0.06
3	600	597	0.69	0.11
4	700	595	0.69	0.09

EXAMPLE A-4

In order to examine the effect of addition of P and/or Sb to SnO₂ as a negative electrode active material, the same test as in Run No. 2 of Example A-1 was conducted, except for using Sb (10 mol%)-added SnO₂, P (10 mol%)-added SnO₂, or Sb + P (10 mol% in total)-added SnO₂ as a negative electrode active material precursor. The calcination of the raw material was conducted in air at 700°C, 300°C or 700°C, respectively, for 4 hours. The results obtained are shown in Table A-4.

For addition of Sb, SbCl₅ or Sb₂O₃ was added at the time of synthesizing Sn(OH)₄. Since SbCl₅ and Sb₂O₃ gave substantially the same test results, the results of SbCl₅ addition are shown. For addition of P, P₂O₅ was added at the time of synthesizing Sn(OH)₄. In experiments using Sb-SnO₂, reduction of the amount of the conducting agents produced no difference in test results so that the results obtained in using a negative electrode active material mixture comprising 91% of the negative electrode active material precursor, 3% of acetylene black, and 6% of polyvinylidene fluoride are shown in Table A-4.

TABLE A-4

Run No.	Additive	(b) (mAh/g)	(c) (V)	(d)
1	none	499	0.68	0.05
2	Sb	575	0.76	0.11
3	P	387	0.72	0.06
4	Sb + P	538	0.72	0.09

EXAMPLE A-5

The same test as in Run No. 1 of Example A-2 was conducted, except for using each of the positive electrode active materials shown in Table A-5. The charging and discharging conditions were 4.3 to 2.7 V. The results obtained are shown in Table A-5.

TABLE A-5

Run No.	Positive Electrode Active Material	(b) (mAh/g)	(c) (V)	(d)
1	LiCoO ₂	485	3.52	0.08
2	LiNiO ₂	522	3.43	0.07
3	LiCo _{0.95} V _{0.05} O _{2.0}	473	3.53	0.06
4	LiMn ₂ O ₄	392	3.56	0.09

EXAMPLE A-6

A mixture of 86% of SnO or SnO₂ as a negative electrode active material precursor, 6% of flake graphite, and 3% of acetylene black was mixed with 4% of an aqueous dispersion of a styrene-butadiene rubber and 1% of carboxymethyl cellulose as binders. The mixture was kneaded using water as a medium to prepare a slurry. The slurry was extrusion coated on both sides of a 18 μm thick copper foil and, after drying, compressed by calendering. The compressed sheet was cut to a prescribed size to prepare a 124 μm thick negative electrode sheet.

A mixture of 87% of LiCoO₂ as a positive electrode active material, 6% of flake graphite, 3% of acetylene black, and, as binders, 3% of an aqueous dispersion of polytetrafluoroethylene and 1% of sodium polyacrylate was kneaded with water, and the resulting slurry was applied on both sides of a 20 μm thick aluminum foil, dried, compressed, and cut to size in the same manner as described above to prepare a 220 μm thick positive electrode sheet.

A nickel or aluminum lead was connected by spot welding to the end of the negative electrode sheet or the positive electrode sheet, respectively. Both the electrode sheets with a lead were dried at 150 °C for 2 hours in dry air having a dew point of not higher than -40 °C.

Dried positive electrode sheet (8), finely porous polypropylene film separator (Cell Guard 2400) (10), dried negative electrode sheet (9), and separator (10) were laminated in this order and rolled up by means of a winder.

The roll was put in cylindrical open-top battery case (11) made of nickel-plated iron which also served as a negative electrode terminal, and a 1 mol/l LiPF₆ solution in a 2:2:6 (by volume) mixture of ethylene carbonate, butylene carbonate, and dimethyl carbonate was poured into the case. Battery cover (12) having a positive electrode terminal was fitted into the top of case (11) via gasket (13) to prepare a cylindrical battery. Positive electrode terminal (12) and positive electrode sheet (8) were previously connected through a lead terminal, and battery case (11) and negative electrode sheet (9) were connected in the same way.

The cross section of the thus assembled cylindrical battery is shown in Fig. 3. Numeral (14) is a safety valve. The charging and discharging conditions were 4.3 to 2.7 V and 1 mA/cm². The results obtained are shown in Table A-6.

TABLE A-6

Run No.	(b) (mAh/g)	(c) (V)	(d)	(e) (mAh/ml)
1	460	3.54	0.04	357

COMPARATIVE EXAMPLE A-1

An electrode pellet was prepared in the same manner as in Run No. 1 of Example A-1 except for replacing the compound as a negative electrode active material with rutile type WO₂ or spinel type Fe₃O₄. The same charge and discharge test as in Example A-2 was conducted. The results obtained are shown in

Table A-7.

TABLE A-7

Run No.	Comparative Compound	(b) (mAh/g)	(c) (V)	(d)
1	WO ₂	163	3.21	0.15
2	Fe ₂ O ₃	109	3.16	0.44

COMPARATIVE EXAMPLE A-2

The coin battery prepared in Run No. 1 of Example A-1 was tested in the same manner as in Example A-1, except for changing the current density for lithium intercalation to 0.38 mA/cm². The results are shown in Table A-8.

TABLE A-8

Run No.	Current Density for Li Intercalation	(b) (mAh/g)	(c) (V)	(d)
1	0.38	233	0.68	0.82

EXAMPLE A-7 AND COMPARATIVE EXAMPLE A-3

A coin battery was prepared in the same manner as in Example A-2, except for using SnO or SnO₂ as a negative electrode active material precursor. Fifty batteries for each negative electrode active material were tested by repeating charging and discharging 20 times at a current density of 5 mA/cm² and then disassembled. The negative electrode pellet was taken out to 60% RH air and observed whether spontaneous ignition would occur.

For comparison, the same test was conducted, except for using a pellet (15 mm in diameter; 100 mg in weight) of an Li-Al alloy as a negative electrode active material.

On comparing Examples A-1 to A-6 with Comparative Example A-1, it was proved that the batteries using the compounds according to the present invention have a high discharge potential, satisfactory charge and discharge cycle characteristics, and a high discharge capacity.

Further, the negative electrode active material precursors of the present invention have a higher pellet density than that of a calcined carbonaceous material (1.1 to 1.4). In particular, SnO or SnO₂ has a pellet density of 3.0 to 3.5, which is about 2 to 3 times that of the latter, and also has about 2.5 times as high discharge capacity per unit weight as the latter. Because the molecular weight per equivalent of the former is twice that of the latter, it is seen that the discharge capacity per volume of the negative electrode active material according to the present invention is about 4 times that of the calcined carbonaceous material.

As a result of the safety test in Example A-7 and Comparative Example A-3, neither the SnO pellet nor the SnO₂ pellet ignited, whereas 32 out of 50 negative electrode pellets of Comparative Example A-3 spontaneously ignited. It is thus seen that the compounds of the present invention are of high safety.

As demonstrated above, the use of an Li-containing transition metal oxide as a positive electrode active material and an oxide mainly comprising at least one of the group IIIB, IVB and VB metals as a negative electrode active material provides a safe nonaqueous secondary battery having a high discharge potential, a high discharge capacity, and satisfactory charge and discharge cycle characteristics.

SYNTHESIS EXAMPLE B-1

Tin monoxide (13.5 g) and silicon dioxide (6.0 g) were dry blended, put in an alumina crucible, heated up to 1000°C at a rate of 10°C/min in an argon atmosphere, calcined at that temperature for 12 hours, cooled to room temperature at a rate of 6°C/min, and taken out of the calcination furnace to obtain SnSiO₃. The calcined product was coarsely ground and further pulverized in a jet mill to an average particle size of 5 μm (hereinafter designated as compound B-1-A).

In the same manner, the following compounds were synthesized starting with the stoichiometric amounts of the respective raw materials.

- SnGeO₃ (compound B-1-B)
- SnPbO₃ (compound B-1-C)
- 5 SnSi_{0.9}Ge_{0.1}O₃ (compound B-1-D)
- SnSi_{0.9}Pb_{0.1}O₃ (compound B-1-E)
- SnSi_{0.5}Ge_{0.5}O₃ (compound B-1-F)
- SnSi_{0.5}Pb_{0.5}O₃ (compound B-1-G)
- SnGe_{0.9}Pb_{0.1}O₃ (compound B-1-H)
- 10 SnSi_{0.7}O_{2.4} (compound B-1-I)
- SnSi_{1.2}O_{3.4} (compound B-1-J)
- SnSi_{1.5}O₄ (compound B-1-K)
- PbSiO₃ (compound B-1-L)
- PbGeO₃ (compound B-1-M)
- 15 PbSi_{0.9}Ge_{0.1}O₃ (compound B-1-N)

SYNTHESIS EXAMPLE B-2

Tin monoxide (13.5 g) and silicon dioxide (6.0 g) were dry blended, put in an alumina crucible, heated up to 1000 °C at a rate of 10 °C/min in an argon atmosphere, calcined at that temperature for 12 hours, and spread on a stainless steel foil in an argon atmosphere for quenching. The resulting product was coarsely ground and further pulverized in a jet mill to obtain SnSiO₃ having an average particle size of 5 μm (hereinafter designated as compound B-2-A).

SYNTHESIS EXAMPLE B-3

Tin dioxide (15.1 g) and silicon dioxide (0.6 g) were dry blended, put in an alumina crucible, calcined at 1000 °C for 12 hours in air, cooled to room temperature, and taken out of the calcination furnace to obtain SnSi_{0.1}O_{2.2}. The calcined product was pulverized in a jet mill to an average particle size of 4 μm (hereinafter designated as compound B-3-A).

In the same manner, the following compounds were synthesized starting with the stoichiometric amounts of the respective raw materials.

- SnSi_{0.3}O_{2.6} (compound B-3-B)
- SnGe_{0.1}O_{2.2} (compound B-3-C)
- 35 SnGe_{0.3}O_{2.6} (compound B-3-D)
- SnPb_{0.1}O_{2.2} (compound B-3-E)
- SnPb_{0.1}O_{2.6} (compound B-3-F)
- SnSi_{0.1}Ge_{0.1}O_{2.4} (compound B-3-G)
- SnSi_{0.1}Pb_{0.1}O_{2.4} (compound B-1-H)
- 40 SnSi_{0.01}O_{2.02} (compound B-3-I)
- SnSi_{1.5}O₅ (compound B-3-J)
- SnSi₂O₆ (compound B-3-K)
- PbSi_{0.1}O_{2.2} (compound B-3-L)
- PbGe_{0.3}O_{2.6} (compound B-3-M)
- 45 GeSi_{0.1}O_{2.2} (compound B-3-N)
- GeSi_{0.3}O_{2.6} (compound B-3-O)

SYNTHESIS EXAMPLE B-4

Tin monoxide (13.5 g) and silicon dioxide (0.6 g) were dry blended, put in an alumina crucible, calcined at 350 °C for 6 hours in an argon atmosphere, cooled to room temperature, and taken out of the calcination furnace to obtain SnSi_{0.1}O_{1.2}. The calcined product was pulverized in a jet mill to an average particle size of 2 μm (compound B-4-A).

In the same manner, the following compounds were synthesized starting with the stoichiometric amounts of the respective raw materials.

- SnSi_{0.01}O_{1.02} (compound B-4-B)
- SnGe_{0.1}O_{1.2} (compound B-4-C)
- SnPb_{0.1}O_{1.2} (compound B-4-D)

PbSi_{0.05}O_{1.1} (compound B-4-E)

PbGe_{0.1}O_{1.1} (compound B-4-F)

GeSiO₃ (compound B-4-G)

5 EXAMPLE B-1

A coin lithium battery having the structure shown in Fig. 2 was assembled in a dry box (dry air; dew point: -40 ° to -70 ° C) using the following materials.

10 Electrode

A negative electrode active material mixture consisting of 82% of each of compounds B-1-A to N synthesized in Synthesis Example B-1, 8% of flake graphite and 4% of acetylene black as conducting agents, and 6% of polyvinylidene fluoride as a binder was compression molded to obtain a negative
15 electrode pellet of 13 mm in diameter and 22 mg in weight. Before use, the pellet was dried in the above-described dry box by means of a far infrared heater at 150 ° C for 3 hours.

Counter Electrode:

20 A positive electrode active material mixture consisting of 82% of LiCoO₂ as a positive electrode active material, 8% of flake graphite, 4% of acetylene black, and 6% of tetrafluoroethylene was compression molded to obtain a pellet of 13 mm in diameter. The weight of the pellet was decided according to the lithium intercalation capacity of the negative electrode active material precursor, and the charge capacity of LiCoO₂ was 170 mAh/g. Before use, the pellet was dried in the same dry box as used above at 150 ° C for 3
25 hours by means of a far infrared heater.

Collector:

A 80 μm thick net of SUS316 was welded to each of the positive electrode case and the negative
30 electrode case.

Electrolytic Solution:

200 μl of a 1 mol/l solution of LiPF₆ in a 2:2:6 (by volume) mixture of ethylene carbonate, butylene
35 carbonate and dimethyl carbonate.

Separator:

A finely porous polypropylene sheet and polypropylene nonwoven fabric impregnated with the electro-
40 lytic solution.

The resulting lithium battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm², a cut-off voltage of 4.3 V in charging, and a cut-off voltage of 2.7 V in discharging. All the tests were started with charging. The results obtained are shown in Table B-1.

Symbols used in Table B-1 and Tables B-2 to B-7 hereinafter described have the following meanings:

- 45 (a) ... negative electrode active material of the present invention
- (b) ... discharge capacity of the first cycle (mAh/g-negative electrode active material)
- (c) ... average discharge potential (V)
- (d) ... cycle characteristics (the number of the cycles at which the discharge capacity was reduced to 60% of that of the first cycle)

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TABLE B-1

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	B-1-A	488	3.51	327
2	B-1-B	448	3.54	289
3	B-1-C	495	3.35	305
4	B-1-D	468	3.56	295
5	B-1-E	483	3.39	317
6	B-1-F	465	3.55	301
7	B-1-G	506	3.40	330
8	B-1-H	440	3.50	267
9	B-1-I	425	3.48	213
10	B-1-J	449	3.52	252
11	B-1-K	437	3.50	167
12	B-1-L	415	3.21	239
13	B-1-M	389	3.25	248
14	B-1-N	378	3.22	182

The results in Table B-1 reveal that the negative electrode active material according to the present invention provides a nonaqueous secondary battery having excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

EXAMPLE B-2

A coin battery was prepared and tested in the same manner as in Run No. 1 of Example B-1, except for replacing compound B-1-A as a negative electrode active material with compound B-2-A synthesized in Synthesis Example B-2. The results obtained are shown in Table B-2.

TABLE B-2

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	B-2-A	521	3.52	351

It is seen that the battery using the negative electrode active material obtained by calcination followed by quenching exhibits further improved charge and discharge cycle characteristics with a high discharge potential and a high capacity.

EXAMPLE B-3

Coin batteries were prepared and tested in the same manner as in Example B-1, except for replacing the compound B-1 as a negative electrode active material with each of compounds B-3-A to B-3-O synthesized in Synthesis Example B-3. The results obtained are shown in Table B-3.

TABLE B-3

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	B-3-A	442	3.50	186
2	B-3-B	448	3.52	185
3	B-3-C	458	3.53	166
4	B-3-D	472	3.51	158
5	B-3-E	481	3.47	161
6	B-3-F	482	3.42	159
7	B-3-G	463	3.55	177
8	B-3-H	468	3.44	180
9	B-3-I	440	3.48	155
10	B-3-J	428	3.54	137
11	B-3-K	444	3.55	142
12	B-3-L	485	3.34	141
13	B-3-M	401	3.38	155
14	B-3-N	417	3.62	170
15	B-3-O	394	3.65	127

It can be seen that the battery using the negative electrode active material according to the present invention have excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

EXAMPLE B-4

Coin batteries were prepared and tested in the same manner as in Example B-1, except for replacing the compound B-1 as a negative electrode active material with each of compounds B-4-A to B-4-G synthesized in Synthesis Example B-4. The results obtained are shown in Table B-4.

TABLE B-4

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	B-4-A	485	3.53	127
2	B-4-B	487	3.53	113
3	B-4-C	472	3.55	141
4	B-4-D	492	3.49	155
5	B-4-E	445	3.32	106
6	B-4-F	428	3.28	116
7	B-5-G	418	3.33	112

It can be seen that the battery using the negative electrode active material according to the present invention has excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

COMPARATIVE EXAMPLE B-1

A coin battery was prepared and tested in the same manner as in Example B-1, except for replacing the compound B-1 as a negative electrode active material with SnO₂ or SnO. The results obtained are shown in Table B-5.

TABLE B-5

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	SnO ₂	443	3.48	85
2	SnO	483	3.53	73

It is seen that the use of the tin compound oxide according to the present invention as a negative electrode active material provides a battery superior to that using SnO₂ or SnO in terms of charge and discharge cycle characteristics and capacity.

COMPARATIVE EXAMPLE B-2

A coin battery was prepared and tested in the same manner as in Example B-1, except for replacing the compound B-1 as a negative electrode active material with WO₂ or Fe₂O₃. The results obtained are shown in Table B-6.

TABLE B-6

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	WO ₂	163	3.21	42
2	Fe ₂ O ₃	109	3.16	13

It is apparent that the use of the tin compound oxide according to the present invention as a negative electrode active material provides a battery superior to that using WO₂ or Fe₂O₃ in terms of all of charge and discharge cycle characteristics, discharge potential, and capacity.

EXAMPLE B-5

A coin battery was prepared and tested in the same manner as in Run No. 1 of Example B-1, except for replacing LiCoO₂ as a positive electrode active material with LiNiO₂, LiCo_{0.95}V_{0.05}O_{2.07} or LiMn₂O₄. The results obtained are shown in Table B-7.

TABLE B-7

Run No.	Positive Electrode Active Material	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	LiCoO ₂	488	3.51	327
2	LiNiO ₂	492	3.41	330
3	LiCo _{0.95} V _{0.05} O _{2.0}	480	3.50	385
4	LiMn ₂ O ₄	470	3.55	323

It is seen that the battery according to the present invention is excellent in all of charge and discharge cycle characteristics, discharge potential, and discharge capacity regardless of which of the above positive electrode active materials is used.

EXAMPLE B-6

A mixture of 86% of compound B-1-A synthesized in Synthesis Example B-1 as a negative electrode active material, 6% of flake graphite, and 3% of acetylene black was mixed with 4% of an aqueous dispersion of a styrene-butadiene rubber and 1% of carboxymethyl cellulose as binders. The mixture was kneaded together with water to prepare a slurry. The slurry was extrusion coated on both sides of a 18 μm thick copper foil and, after drying, compressed by calendaring. The compressed sheet was cut to a prescribed size to prepare a 124 μm thick negative electrode sheet.

A mixture of 87% of LiCoO₂ as a positive electrode active material, 6% of flake graphite, 3% of acetylene black, and, as binders, 3% of an aqueous dispersion of polytetrafluoroethylene and 1% of sodium

polyacrylate was kneaded with water, and the resulting slurry was applied on both sides of a 20 μm thick aluminum foil, dried, compressed, and cut to size in the same manner as described above to prepare a 220 μm thick positive electrode sheet.

A nickel or aluminum lead was connected by spot welding to the end of the negative electrode sheet or the positive electrode sheet, respectively. Both the electrode sheets with a lead were dried at 150 °C for 2 hours in dry air having a dew point of not higher than -40 °C.

Dried positive electrode sheet (8), finely porous polypropylene film separator (Cell Guard 2400) (10), dried negative electrode sheet (9), and separator (10) were laminated in this order and rolled up by means of a winder.

The roll was put in cylindrical open-top battery case (11) made of nickel-plated iron which also served as a negative electrode terminal, and a 1 mol/l LiPF_6 solution in a 2:2:6 (by volume) mixture of ethylene carbonate, butylene carbonate, and dimethyl carbonate was poured into the case. Battery cover (12) with a positive electrode terminal was fitted into the top of case (11) via gasket (13) to prepare a cylindrical battery. Positive electrode terminal (12) and positive electrode sheet (8) were previously connected via a lead terminal, and battery case (11) and negative electrode sheet (9) were connected in the same way.

The cross section of the thus assembled cylindrical battery is shown in Fig. 3. Numeral (14) is a safety valve. The battery was subjected to a charge and discharge test under conditions of 4.3 to 2.7 V and 1 mA/cm^2 . The results obtained are shown in Table B-8. In Table B-8, symbol (e) means a discharge capacity per ml of a C size battery.

TABLE B-8

Run No.	(b) (mAh/g)	(c) (V)	(d) (cycles)	(e) (mAh/ml)
1	490	3.54	550	360

EXAMPLE B-8 AND COMPARATIVE EXAMPLE B-3

Fifty coin batteries were prepared in the same manner as in Run No. 1 of Example B-1 and subjected to a safety test in the same manner as in Example A-7. As a result, none of them ignited.

For comparison, the same test was conducted, except for using a pellet (15 mm in diameter; 100 mg in weight) prepared by using an Li-Al (80%-20%) alloy as a negative electrode active material. As a result, 32 out of 50 ignited.

It can be seen from these results that the nonaqueous secondary battery according to the present invention is of high safety.

As described above, the nonaqueous secondary battery of the present invention in which an Li-containing transition metal oxide is used as a positive electrode active material and at least one specific compound oxide as a negative electrode active material exhibits a high discharge potential, a high discharge capacity, excellent charge and discharge cycle characteristics, and high safety.

In the following Examples, SnO , GeO , GeO_2 , SiO_2 , PbO , PbO_2 , Pb_2O_3 , Pb_3O_4 , Sb_2O_3 , Sb_2O_4 , Bi_2O_3 , WO_2 (comparative), and Fe_2O_3 (comparative) used as a negative electrode active material are commercially available ones.

SYNTHESIS EXAMPLE C-1

Tin chloride and sodium hydroxide were reacted in an aqueous solution to precipitate $\text{Sn}(\text{OH})_4$. The precipitate was calcined in air at 400 °C for 4 hours to synthesize rutile type SnO_2 , which was ground in a mortar to an average primary particle size of about 0.05 μm .

SYNTHESIS EXAMPLE C-2

Lithium carbonate (7.3 g) and tin dioxide (15.1 g) were dry blended, put in an aluminum crucible, and calcined in air at 1000 °C for 12 hours. After the calcination, the product was cooled to room temperature to obtain Li_2SiO_3 .

In the same manner, Li_2GeO_3 , Li_2PbO_3 , Li_3BiO_4 , Li_3SbO_4 , Li_2ZnO_2 , Li_3InO_3 , $\text{Li}_2\text{ZnSn}_2\text{O}_6$, $\text{Li}_2\text{MgSn}_2\text{O}_6$, $\text{Li}_{0.1}\text{SnO}_{2.05}$, Li_4SnO_4 , Li_6SnO_5 , and Li_8SnO_6 were prepared using stoichiometrical amounts of the respective starting materials.

SYNTHESIS EXAMPLE C-3

Lithium acetate dihydrate (10.2 g) and tin monoxide (13.5 g) were dry blended, put in a porcelain crucible, calcined in an argon atmosphere at 350 °C for 24 hours, and cooled to room temperature to synthesize Li_2SnO_2 . The product was pulverized in a jet mill to an average particle size of 2.5 μm .

In the same manner, $\text{Li}_{0.1}\text{SnO}_{1.05}$, Li_6SnO_4 , and Li_8SnO_5 were synthesized using stoichiometrical amounts of the respective starting materials.

SYNTHESIS EXAMPLE C-4

Silicon dioxide (2.60 g) and tin monoxide (1.16 g) were dry blended, put in an alumina crucible, calcined in air at 1000 °C for 12 hours, and rapidly cooled to room temperature to synthesize amorphous and glassy SiSnO_3 .

SYNTHESIS EXAMPLE C-5

Lithium carbonate (2.26 g), tricobalt tetroxide (5.0 g), and germanium dioxide (0.19 g) were dry blended and calcined in air at 900 °C for 18 hours to synthesize crystalline $\text{LiCoGe}_{0.03}\text{O}_2$. Average particle size: 4 μm .

SYNTHESIS EXAMPLE C-6

Lithium carbonate (2.26 g), tricobalt tetroxide (5.0 g), and zirconium dioxide (0.16 g) were dry blended, and calcined in air at 900 °C for 18 hours to synthesize crystalline $\text{LiCoZr}_{0.02}\text{O}_2$. Average particle size: 5 μm .

SYNTHESIS EXAMPLE C-7

Lithium carbonate (2.26 g), tricobalt tetroxide (5.0 g), germanium dioxide (0.13 g), and zirconium dioxide (0.16 g) were dry blended, and calcined in air at 900 °C for 18 hours to synthesize crystalline $\text{LiCoGe}_{0.02}\text{Zr}_{0.02}\text{O}_2$. Average particle size: 4 μm .

In the same manner, $\text{LiCoGe}_{0.06}\text{O}_2$, $\text{LiCoGe}_{0.06}\text{O}_2$, $\text{LiCoZr}_{0.06}\text{O}_2$, $\text{LiCoZr}_{0.08}\text{O}_2$, $\text{LiCoTi}_{0.08}\text{O}_2$, and $\text{LiCoTi}_{0.03}\text{O}_2$ were synthesized as a positive electrode active material by using stoichiometrical amounts of the respective starting materials.

SYNTHESIS EXAMPLE C-8

Lithium carbonate (2.26 g) and tricobalt tetroxide (5.0 g) were dry blended and calcined in air at 900 °C for 18 hours to synthesize crystalline LiCoO_2 . Average particle size: 5 μm .

SYNTHESIS EXAMPLE C-9

Lithium carbonate (1.20 g) and manganese dioxide (5.92 g) were dry blended and calcined in air at 800 °C for 12 hours to synthesize crystalline LiMn_2O_4 . Average particle size: 3 μm .

SYNTHESIS EXAMPLE C-10

Lithium carbonate (2.26 g), tricobalt tetroxide (2.50 g), and nickel oxide (2.29 g) were dry blended and calcined in air at 800 °C for 20 hours to synthesize crystalline $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$. Average particle size: 7 μm .

EXAMPLE C-1

A coin battery was assembled using the following materials.

Electrode:

A negative electrode active material mixture consisting of 82% of a negative electrode active material precursor shown in Table C-1, 8% of flake graphite and 4% of acetylene black as conducting agents, and 6% of polyvinylidene fluoride as a binder was compression molded into a pellet of 13 mm in diameter and

22 mg in weight. Before use, the pellet was dried in a dry box (dry air; dew point: -40 ° to -70 ° C) by means of a far infrared heater at 150 ° C for about 3 hours.

Counter Electrode:

A positive electrode active material mixture consisting of 82% of a positive electrode active material shown in Table C-1, 8% of flake graphite and 4% of acetylene black as conducting agents, and 6% of tetrafluoroethylene as a binder was compression molded into a pellet of 13 mm in diameter and 110 mg in weight. Before use, the pellet was dried under the same conditions as used for the negative electrode pellet.

Collector:

A 80 µm thick net of SUS316 was welded to each of the positive case and the negative case.

Electrolytic Solution:

200 µl of a 1 mol/l solution of LiPF₆ in a 2:2:6 (by volume) mixed solvent of ethylene carbonate, butylene carbonate and dimethyl carbonate.

Separator:

A finely porous polypropylene sheet and polypropylene nonwoven fabric impregnated with the electrolytic solution.

The resulting lithium battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm², a cut-off voltage of 4.3 V in charging, and a cut-off voltage of 2.7 V in discharging. All the tests were started with intercalation of lithium into the negative electrode active material precursor of the present invention. While more than 100 kinds of coin batteries were prepared and tested using a variety of combinations of a negative electrode active material and a positive electrode active material, the typical results are shown in Table C-1. It should therefore be understood that the combination of a negative electrode active material and a positive electrode active material which can be used in the present invention are not limited to those shown in the Table.

TABLE C-1

	Positive Electrode Active Material	Negative Electrode Active Material	Average Discharge Potential (V)	Discharge Capacity at the 2nd Cycle (mAh/g)	Cycle Charac- teristics*
5					
10	Comparison:				
	LiCoO ₂	WO ₂	3.20	160	0.15
	LiMn ₂ O ₄	WO ₂	3.15	145	0.16
15	LiNi _{0.5} Co _{0.5} O ₂	WO ₂	3.15	140	0.16
	LiCoO ₂	SnO	3.52	480	0.08
20	LiCoO ₂	SnO ₂	3.52	470	0.07
	LiMn ₂ O ₄	SnO	3.50	390	0.09
	LiNi _{0.5} Co _{0.5} O ₂	SnO	3.48	360	0.09
25	LiCoO ₂	SnSiO ₃	3.50	460	0.04
	LiCoO ₂	Li ₂ SnO ₃	3.50	440	0.06
30	LiCoO ₂	GeO ₂	3.46	229	-0.10
	Invention:				
	LiCoGe _{0.03} O ₂	SnO	3.55	490	0.05
35	LiCoGe _{0.06} O ₂	SnO	3.55	482	0.06
	LiCoGe _{0.08} O ₂	SnO	3.53	482	0.06
40	LiCoZr _{0.02} O ₂	SnO	3.55	515	0.05
	LiCoZr _{0.06} O ₂	SnO	3.55	505	0.06
	LiCoZr _{0.08} O ₂	SnO	3.53	500	0.06
45	LiCoGe _{0.03} O ₂	SnSiO ₃	3.55	482	0.03
	LiCoGe _{0.03} O ₂	Li ₂ SnO ₃	3.55	450	0.05
50	LiCoGe _{0.03} O ₂	GeO ₂	3.48	255	-0.10

TABLE C-1 (cont'd.)

	Positive Electrode Active Material	Negative Electrode Active Material	Average Discharge Potential (V)	Discharge Capacity at the 2nd Cycle (mAh/g)	Cycle Charac- teristics*
5					
10	$\text{LiCoZr}_{0.02}\text{O}_2$	SnSiO_3	3.55	490	0.03
	$\text{LiCoZr}_{0.02}\text{O}_2$	Li_2SnO_3	3.55	460	0.05
	$\text{LiCoZr}_{0.02}\text{O}_2$	GeO_2	3.50	265	-0.10
15	$\text{LiCoGe}_{0.02}\text{Zr}_{0.02}\text{O}_2$	SnSiO_3	3.55	485	0.03
	$\text{LiCoGe}_{0.02}\text{Zr}_{0.02}\text{O}_2$	Li_2SnO_3	3.55	455	0.04
20	$\text{LiCoTi}_{0.03}\text{O}_2$	SnO	3.55	482	0.06
	$\text{LiCoTi}_{0.03}\text{O}_2$	SnO	3.54	480	0.05
	$\text{LiCoGe}_{0.03}\text{O}_2$	SnO_2	3.54	475	0.05
25	$\text{LiCoGe}_{0.03}\text{O}_2$	Li_2SnO_2	3.55	490	0.05
	$\text{LiCoGe}_{0.03}\text{O}_2$	$\text{Li}_2\text{MgSn}_2\text{O}_6$	3.54	485	0.06
30	Note: * (Discharge capacity of the 10th cycle - discharge capacity of the 1st cycle)/discharge capacity of the 1st cycle				

SYNTHESIS EXAMPLE C-11

40 Li_2CO_3 and MnO_2 were mixed at a molar ratio of about 1:4, and the mixture was calcined in air at 400°C for 12 hours to synthesize a spinel type lithium-manganese oxide having the composition of $\text{Li}_2\text{Mn}_4\text{O}_9$ (or $\text{Li}_{0.89}\text{Mn}_{1.78}\text{O}_4$) according to the present invention. An oxide of the same composition could also be synthesized by calcining a 1:4 (by mole) mixture of Li_2CO_3 and MnCO_3 in air at 430°C for 5 hours.

SYNTHESIS EXAMPLE C-12

45 Li_2CO_3 and MnO_2 were mixed at a molar ratio of about 0.35:2, and the mixture was calcined in air at 450°C for 12 hours to synthesize a spinel type lithium-manganese oxide having the composition of $\text{Li}_{0.7}\text{Mn}_2\text{O}_4$ according to the present invention.

SYNTHESIS EXAMPLE C-13

50 $\text{Li}_2\text{Mn}_4\text{O}_9$ synthesized in Synthesis Example 11 and $\lambda\text{-MnO}_2$ were mixed at an Li:Mn atomic ratio of about 2:5, and the mixture was calcined in air at 250°C for 24 hours to synthesize a spinel type lithium-manganese oxide having the composition of $\text{Li}_2\text{Mn}_5\text{O}_{11}$ according to the present invention.

SYNTHESIS EXAMPLE C-14

Li_2CO_3 and $\lambda\text{-MnO}_2$ were mixed at an Li:Mn molar ratio of about 4:5, and the mixture was calcined in air at 430 °C for 12 hours to synthesize a lithium-manganese oxide having the composition of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (or $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$) according to the present invention.

SYNTHESIS EXAMPLE C-15

$\text{Li}_4\text{Mn}_5\text{O}_{12}$ synthesized in Synthesis Example C-14 and EMD were mixed at a molar ratio of about 1:10, and the mixture was calcined in air at 400 °C for 40 hours to synthesize a lithium-manganese oxide having the composition of $\text{Li}_{0.5}\text{Mn}_{1.88}\text{O}_4$. Alternatively, the same compound could be obtained by mixing $\text{Li}_4\text{Mn}_5\text{O}_{12}$ with CMD instead of EMD at a molar ratio of 1:10 and calcining the mixture at 400 °C for 24 hours.

SYNTHESIS EXAMPLE C-16

$\text{Li}_4\text{Mn}_5\text{O}_{12}$ synthesized in Synthesis Example C-14 and $\lambda\text{-MnO}_2$ were mixed at a molar ratio of about 1:12, and the mixture was calcined in air at 400 °C for 12 hours to synthesize a lithium-manganese oxide having the composition of $\text{Li}_{0.46}\text{Mn}_{1.89}\text{O}_4$ according to the present invention.

The manganese oxides synthesized in Synthesis Examples C-11 to C-16 are represented by $\text{Li}_2\text{O} \cdot (\text{MnO}_2)_x$ in which x falls within a range of 2 to 9.

EXAMPLE C-2

A positive electrode pellet (active material content: 16.4 mg) and a negative electrode pellet (active material content: 85 mg) were prepared in the same manner as in Example C-1, except for using the active materials shown in Table C-2.

A 80 μm thick net of SUS316 as a collector was welded to each of positive and negative cases.

As an electrolytic solution, 250 μl of a 1 mol/l solution of LiPF_6 in a 1:1 (by volume) mixed solvent of ethylene carbonate and diethylene carbonate was infiltrated into a separator composed of a finely porous polypropylene sheet and polypropylene nonwoven fabric. The positive electrode pellet and the negative electrode pellet was set on the respective collector, and the positive electrode case and the negative electrode case were fitted to each other with the separator therebetween in a dry box to prepare a coin lithium battery.

The resulting lithium battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm^2 , a cut-off voltage of 4.3 V in charging, and a cut-off voltage of 2.7 V in discharging. All the tests were started from charging. The results obtained are shown in Table C-2. In the Table, "discharge capacity" means the capacity per unit weight of the negative electrode active material up to the time when the discharge was terminated at 1.8 V, and "capacity cycle characteristics" means the number of cycles required for the discharge capacity to be reduced to 60% of the initial discharge capacity.

TABLE C-2

	Positive Electrode Active Material	Negative Electrode Active Material	Discharge Capacity of the 2nd Cycle (mAh/g)	Average Discharge Potential (V)	Capacity Cycle Charac- teristics (cycles)
5					
10	Comparison:				
	LiMn_2O_4	WO_2	170	3.15	40
	$\text{Li}_{0.46}\text{Mn}_{1.89}\text{O}_4$	WO_2	180	3.20	50
15	LiMn_2O_4	SnO_2	410	3.45	130
	LiMn_2O_4	SnO	430	3.45	120
20	LiMn_2O_4	Li_2SnO_3	420	3.45	125
	LiMn_2O_4	SnSiO_3	425	3.46	135
	Invention:				
25	$\text{Li}_2\text{Mn}_5\text{O}_{11}$	SnO_2	430	3.50	130
	$\text{Li}_2\text{Mn}_5\text{O}_{11}$	SnO	450	3.50	122
30	$\text{Li}_2\text{Mn}_5\text{O}_{11}$	Li_2SnO_3	440	3.50	130
	$\text{Li}_2\text{Mn}_5\text{O}_{11}$	SnSiO_3	445	3.52	135
	$\text{Li}_2\text{Mn}_4\text{O}_9$	SnO	445	3.50	120
35	$\text{Li}_{0.46}\text{Mn}_{1.89}\text{O}_4$	SnO	455	3.50	120
	$\text{Li}_{0.5}\text{Mn}_{1.88}\text{O}_4$	SnO	450	3.50	120
40	$\text{Li}_{0.38}\text{Mn}_{1.9}\text{O}_4$	SnO	460	3.50	120
	$\text{Li}_2\text{Mn}_4\text{O}_9$	SnSiO_3	440	3.52	150
	$\text{Li}_{0.46}\text{Mn}_{1.89}\text{O}_4$	SnSiO_3	450	3.52	155
45	$\text{Li}_{0.5}\text{Mn}_{1.88}\text{O}_4$	SnSiO_3	445	3.53	150
	$\text{Li}_{0.38}\text{Mn}_{1.9}\text{O}_4$	SnSiO_3	455	3.52	155
50	$\text{Li}_{0.46}\text{Mn}_{1.89}\text{O}_4$	Li_2SnO_3	435	3.50	145

55

TABLE C-2 (cont'd.)

	Positive Electrode Active Material	Negative Electrode Active Material	Discharge Capacity of the 2nd Cycle (mAh/g)	Average Discharge Potential (V)	Capacity Cycle Charac- teristics (cycles)
5					
10	$\text{Li}_{0.43}\text{Mn}_{1.89}\text{O}_4$	Li_2SnO_3	440	3.50	145
	$\text{Li}_{0.5}\text{Mn}_{1.88}\text{O}_4$	Li_2SnO_2	450	3.50	140
	$\text{Li}_2\text{Mn}_5\text{O}_{11}$	GeO_2	250	3.40	200
15	$\text{Li}_{0.46}\text{Mn}_{1.89}\text{O}_4$	GeO_2	270	3.40	210

The results in Table C-2 prove that the lithium ion nonaqueous secondary batteries prepared from a combination of the negative electrode active material according to the present invention and a spinel type lithium-manganese double oxide as a positive electrode active material are superior in discharge capacity and cycle characteristics to conventional batteries using a combination of a metal oxide type negative electrode active material and a manganese oxide as a positive electrode active material.

The negative electrode active material according to the present invention can be obtained by electrochemically intercalating lithium ions into an oxide (a negative electrode active material precursor). The lithium intercalation is effected until the basic structure of the precursor is changed (for example, until the X-ray diffraction pattern changes) and also until the thus changed basic structure of the Li ion-containing oxide undergoes substantially no change during charging and discharging (for example, the X-ray diffraction pattern of the Li-containing oxide does not change substantially). The change in basic structure means change from a certain crystal structure to a different crystal structure or from a crystal structure to an amorphous structure.

The lithium nonaqueous secondary batteries in which an oxide of a metal selected from the group IIIB, IVB and VB elements is used as a negative electrode active material and a compound oxide containing cobalt and a metal selected from the group IIIB, IVB and VB elements or a spinel type lithium-manganese compound oxide is used as a positive electrode active material have a high discharge capacity and a high charging and discharging efficiency as well as high safety and satisfactory cycle characteristics owing to the properties of the negative electrode active material. In addition, use of inexpensive manganese brings about an economical advantage.

40 SYNTHESIS EXAMPLE D-1

Tin monoxide (13.5 g) and silicon dioxide (6.0 g) were dry blended, put in an alumina crucible, heated up to 1000°C at a rate of 15°C/min in an argon atmosphere, calcined at that temperature for 12 hours, cooled to room temperature at a rate of 10°C/min, and taken out of the calcination furnace to obtain SnSiO_3 . The calcined product was pulverized in a jet mill to an average particle size of 4.5 μm (hereinafter designated as compound D-1-A).

The X-ray diffraction pattern ($\text{CuK}\alpha$ rays) of compound D-1-A is shown in Fig. 1. The pattern shows a broad peak centered at about 28° (2θ) with no diffraction assigned to crystal properties between 40° and 70° (2θ).

The following compounds were also synthesized in the same manner as described above using stoichiometrical amounts of the respective starting materials. The X-ray diffraction pattern ($\text{CuK}\alpha$ rays) of these compounds similarly exhibited a broad scattering band with its peak between 20° and 40° (2θ). The diffraction intensity of the peak of the broad scattering band appearing between 20° and 40° (2θ) is taken as A, and the strongest intensity of any diffraction line assigned to crystal properties which may appear between 40° and 70° (2θ) is taken as B (B = 0 where no diffraction assigned to crystal properties occurs). The B/A value is shown together with the compound number.

SnGeO_3 (compound D-1-B; B/A = 0)

$\text{SnSi}_{0.8}\text{P}_{0.1}\text{O}_3$ (compound D-1-C; B/A = 0)

- $\text{SnSi}_{0.9}\text{Ge}_{0.1}\text{O}_3$ (compound D-1-D; B/A = 0)
 $\text{SnSi}_{0.9}\text{Pb}_{0.1}\text{O}_3$ (compound D-1-E; B/A = 0)
 $\text{SnSi}_{0.5}\text{Ge}_{0.6}\text{O}_3$ (compound D-1-F; B/A = 0)
 $\text{SnSi}_{0.5}\text{Pb}_{0.5}\text{O}_3$ (compound D-1-G; B/A = 0.3)
5 $\text{SnGe}_{0.9}\text{Pb}_{0.1}\text{O}_3$ (compound D-1-H; B/A = 0)
 $\text{SnSi}_{0.8}\text{O}_{2.4}$ (compound D-1-I; B/A = 0.1)
 $\text{SnSi}_{1.2}\text{O}_{3.4}$ (compound D-1-J; B/A = 0)
 $\text{SnSi}_{1.5}\text{O}_4$ (compound D-1-K; B/A = 0)
 PbSiO_3 (compound D-1-L; B/A = 0)
10 PbGeO_3 (compound D-1-M; B/A = 0)
 $\text{PbSi}_{0.9}\text{Ge}_{0.1}\text{O}_3$ (compound D-1-N; B/A = 0)
 $\text{SnPO}_{3.5}$ (compound D-1-O; B/A = 0)
 $\text{SnBO}_{2.5}$ (compound D-1-P; B/A = 0)
 $\text{SnSi}_{0.9}\text{O}_{2.8}$ (compound D-1-Q; B/A = 0)

15

SYNTHESIS EXAMPLE D-2

- Tin monoxide (1.35 g) and silicon dioxide (0.6 g) were dry blended, put in an alumina crucible, heated up to 1000 °C at a rate of 15 °C/min in an argon atmosphere, calcined at that temperature for 10 hours, and
 20 quenched by spreading on a stainless steel foil in an argon atmosphere. The calcined product (SnSiO_3) was coarsely ground and then pulverized in a jet mill to an average particle size of 3.5 μm (hereinafter designated as compound D-2-A). The B/A ratio in the X-ray diffraction pattern was 9.5.

SYNTHESIS EXAMPLE D-3

25

Tin dioxide (15.1 g) and silicon dioxide (0.6 g) were dry blended, put in an alumina crucible, calcined at 1200 °C for 10 hours, cooled to room temperature, and taken out of the furnace to obtain $\text{SnSi}_{0.1}\text{O}_{2.2}$. The calcined product was pulverized in a jet mill to an average particle size of 4 μm (hereinafter designated as compound D-3-A). The B/A ratio in the X-ray diffraction pattern was 0.

- 30 In the same manner as above, the following compounds were synthesized using stoichiometrical amounts of the respective starting materials.

- $\text{SnSi}_{0.3}\text{O}_{2.8}$ (compound D-3-B; B/A = 2.4)
 $\text{SnGe}_{0.1}\text{O}_{2.2}$ (compound D-3-C; B/A = 7.4)
 $\text{SnGe}_{0.3}\text{O}_{2.6}$ (compound D-3-D; B/A = 4.7)
 35 $\text{SnPb}_{0.1}\text{O}_{2.2}$ (compound D-3-E; B/A = 7.5)
 $\text{SnPb}_{0.1}\text{O}_{2.8}$ (compound D-3-F; B/A = 16.5)
 $\text{SnSi}_{0.1}\text{Ge}_{0.1}\text{O}_{2.4}$ (compound D-3-G; B/A = 9.5)
 $\text{SnSi}_{0.1}\text{Pb}_{0.1}\text{O}_{2.4}$ (compound D-3-H; B/A = 29.1)
 $\text{SnSi}_{0.01}\text{O}_{2.02}$ (compound D-3-I; B/A = 7.1)
 40 $\text{SnSi}_{1.3}\text{O}_5$ (compound D-3-J; B/A = 0)
 SnSi_2O_6 (compound D-3-K; B/A = 0)
 $\text{PbSi}_{0.1}\text{O}_{2.2}$ (compound D-3-L; B/A = 5.3)
 $\text{PbGe}_{0.3}\text{O}_{2.6}$ (compound D-3-M; B/A = 2.3)
 $\text{GeSi}_{0.1}\text{O}_{2.2}$ (compound D-3-N; B/A = 0)
 45 $\text{GeSi}_{0.2}\text{O}_{2.6}$ (compound D-3-O; B/A = 0)
 $\text{SnP}_{0.3}\text{O}_{2.75}$ (compound D-3-P; B/A = 1.4)
 $\text{SnB}_{0.3}\text{O}_{2.45}$ (compound D-3-Q; B/A = 6.4)

SYNTHESIS EXAMPLE D-4

50

- Tin monoxide (13.5 g), 4.8 g of silicon dioxide, and 1.42 g of diphosphorus pentoxide, each weighed in dry air having a dew point of -50 °C, were dry blended in a ball mill in the same dry air. The mixture was put in an alumina crucible, heated to 1100 °C at a rate of 10 °C/min in an argon atmosphere, calcined at that temperature for 10 hours, and cooled to room temperature at a rate of 8.3 °C/min to obtain a glassy
 55 compound. The compound was pulverized in a jet mill and air-classified to obtain compound D-4-A having an average particle size of 4 μm . The B/A ratio in the X-ray diffraction pattern was 0.

In the same manner as described above, the following compounds were synthesized using stoichiometrical amounts of the respective starting materials (Al_2O_3 and Sb_2O_3 were used as an Al source

and an Sb source, respectively).

$\text{SnSi}_{0.9}\text{P}_{0.1}\text{O}_{3.05}$ (compound D-4-B; B/A = 0)

$\text{SnSi}_{0.7}\text{P}_{0.9}\text{O}_{3.15}$ (compound D-4-C; B/A = 0)

$\text{SnSi}_{0.5}\text{P}_{0.5}\text{O}_{3.25}$ (compound D-4-D; B/A = 0)

5 $\text{SnSi}_{0.2}\text{P}_{0.8}\text{O}_{3.4}$ (compound D-4-E; B/A = 0)

$\text{SnSi}_{0.8}\text{P}_{0.1}\text{Sb}_{0.1}\text{O}_3$ (compound D-4-F; B/A = 0.5)

SYNTHESIS EXAMPLE D-5

10 Tin monoxide (10.78 g), 3.6 g of silicon dioxide, 4.11 g of stannous pyrophosphate, and 2.1 g of germanium dioxide were dry blended in a ball mill. The mixture was put in an alumina crucible, heated to 1100 °C at a rate of 10 °C/min in an argon atmosphere, and calcined at that temperature for 10 hours. The calcined product was quenched by pouring into water in an argon atmosphere to obtain a glassy compound. The compound was wet ground in a ball mill using water as a grinding medium, and the slurry
15 was passed through a sieve of 25 μm to remove coarse particles. Water was removed by decantation, and the solid was dried at 150 °C for 1 hour to obtain compound D-5-A having an average particle size of 3.1 μm. The B/A ratio in the X-ray diffraction pattern was 0.

In the same manner as described above, the following compounds were synthesized using stoichiometrical amounts of the respective starting materials. Al_2O_3 was used as an aluminum source.

20 $\text{SnSi}_{0.7}\text{Ge}_{0.1}\text{P}_{0.2}\text{O}_{3.1}$ (compound D-5-B; B/A = 0)

$\text{SnSi}_{0.6}\text{Ge}_{0.4}\text{P}_{0.1}\text{O}_{3.25}$ (compound D-5-C; B/A = 0)

$\text{SnSi}_{0.2}\text{Ge}_{0.1}\text{P}_{0.7}\text{O}_{3.35}$ (compound D-5-D; B/A = 0)

$\text{SnSi}_{0.8}\text{P}_{0.1}\text{Al}_{0.1}\text{O}_3$ (compound D-5-E; B/A = 0)

$\text{SnSi}_{0.8}\text{P}_{0.2}\text{Al}_{0.1}\text{O}_{3.25}$ (compound D-5-F; B/A = 0)

25 $\text{SnSi}_{0.6}\text{P}_{0.1}\text{Al}_{0.3}\text{O}_{2.9}$ (compound D-5-G; B/A = 0)

$\text{SnSi}_{0.6}\text{P}_{0.3}\text{Al}_{0.1}\text{O}_{3.1}$ (compound D-5-H; B/A = 0)

$\text{SnSi}_{0.3}\text{P}_{0.7}\text{Al}_{0.1}\text{O}_{3.5}$ (compound D-5-I; B/A = 1.5)

$\text{SnSi}_{0.8}\text{P}_{0.2}\text{O}_{3.1}$ (compound D-5-J; B/A = 0)

$\text{SnSi}_{0.6}\text{P}_{0.4}\text{Al}_{0.2}\text{O}_{3.5}$ (compound D-5-K; B/A = 0)

30 $\text{SnSi}_{0.1}\text{P}_{0.9}\text{Al}_{0.1}\text{O}_{3.6}$ (compound D-5-L; B/A = 0)

$\text{SnSi}_{0.8}\text{Al}_{0.2}\text{P}_{0.2}\text{O}_{3.4}$ (compound D-5-M; B/A = 0)

$\text{SnSi}_{0.7}\text{Al}_{0.2}\text{P}_{0.3}\text{P}_{3.45}$ (compound D-5-N; B/A = 0)

$\text{SnSi}_{0.4}\text{Al}_{0.2}\text{P}_{0.6}\text{O}_{3.6}$ (compound D-5-O; B/A = 0)

$\text{SnPAl}_{0.1}\text{O}_{3.65}$ (compound D-5-P; B/A = 0)

EXAMPLE D-1

A coin-shaped nonaqueous battery having the structure shown in Fig. 2 was assembled in a dry box (dew point: -40 ° to -70 °C; dry air) using the following materials.

Electrode:

A negative electrode active material mixture consisting of 82% of each of compounds D-1-A to D-1-Q synthesized in Synthesis Example D-1, 8% of flake graphite and 4% of acetylene black as conducting agents, and 6% of polyvinylidene fluoride as a binder was compression molded into a pellet of 13 mm in diameter and 22 mg in weight. Before use, the pellet was dried in the above-described dry box by means of
45 a far infrared heater at 150 °C for 3 hours.

Counter Electrode:

50 A positive electrode active material mixture consisting of 82% of LiCoO_2 as a positive electrode active material, 8% of flake graphite, 4% of acetylene black, and 6% of tetrafluoroethylene was compression molded to obtain a pellet of 13 mm in diameter (the weight was decided according to the lithium intercalation capacity of the compound D-1). The charge capacity of LiCoO_2 was 170 mAh/g. Before use,
55 the pellet was dried in the same dry box as used above at 150 °C for 3 hours by means of a far infrared heater.

Collector:

A 80 μm thick net of SUS316 was welded to each of the positive case and the negative case.

5 Electrolytic Solution:

200 μl of a 1 mol/l solution of LiPF_6 in a 2:2:6 (by volume) mixed solvent of ethylene carbonate, butylene carbonate and dimethyl carbonate.

10 Separator:

A finely porous polypropylene sheet and polypropylene nonwoven fabric impregnated with the electrolytic solution.

The resulting nonaqueous battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm^2 and a voltage between 4.3 V and 2.7 V. All the tests were started with charging. The results obtained are shown in Table D-1.

Symbols used in Table D-1 and Tables D-2 to D-10 hereinafter shown have the following meanings:

- (a) ... negative electrode active material of the present invention
- (b) ... discharge capacity of the first cycle (mAh/g -negative electrode active material)
- 20 (c) ... average discharge potential (V)
- (d) ... cycle characteristics (the number of cycles at which the discharge capacity was reduced to 60% of the initial discharge capacity).

TABLE D-1

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Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	D-1-A	493	3.50	335
2	D-1-B	452	3.52	296
3	D-1-C	498	3.30	311
4	D-1-D	470	3.59	300
5	D-1-E	484	3.40	296
6	D-1-F	451	3.59	304
7	D-1-G	430	3.45	224
8	D-1-H	428	3.53	268
9	D-1-I	501	3.47	207
10	D-1-J	453	3.47	311
11	D-1-K	451	3.50	268
12	D-1-L	421	3.29	246
13	D-1-M	395	3.21	262
14	D-1-N	380	3.27	290
15	D-1-O	462	3.54	302
16	D-1-P	472	3.55	288
17	D-1-Q	498	3.44	305

It is seen from these results that the negative electrode active material according to the present invention provides a nonaqueous secondary battery having excellent charge and discharge cycle characteristics with a high discharge potential and a high capacity.

50 EXAMPLE D-2

A coin battery was prepared and tested in the same manner as in Example D-1, except for using compound D-2-A synthesized in Synthesis Example D-2 as a negative electrode active material. The results obtained are shown in Table D-2.

55

TABLE D-2

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	D-2-A	544	3.5	377

It is seen that the battery using the negative electrode active material obtained by calcination followed by quenching exhibits further improved charge and discharge cycle characteristics with a high discharge potential and a high capacity.

EXAMPLE D-3

Coin batteries were prepared and tested in the same manner as in Example D-1, except for replacing the compound D-1 with each of compounds D-3-A to D-3-Q synthesized in Synthesis Example D-3 as a negative electrode active material. The results obtained are shown in Table D-3.

TABLE D-3

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	D-3-A	449	3.48	196
2	D-3-B	453	3.51	197
3	D-3-C	459	3.51	177
4	D-3-D	478	3.53	163
5	D-3-E	487	3.45	169
6	D-3-F	489	3.48	164
7	D-3-G	471	3.51	182
8	D-3-H	475	3.42	155
9	D-3-I	448	3.44	197
10	D-3-J	431	3.50	255
11	D-3-K	409	3.51	251
12	D-3-L	492	3.38	189
13	D-3-M	409	3.42	202
14	D-3-N	421	3.61	279
15	D-3-O	401	3.68	288
16	D-3-P	457	3.40	212
17	D-3-Q	463	3.41	211

It can be seen that the batteries using the negative electrode active material according to the present invention have excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

COMPARATIVE EXAMPLE D-1

A coin battery was prepared and tested in the same manner as in Example D-1, except for using, as a negative electrode active material, SnO₂ or SnO. The SnO₂ and SnO used here showed no broad scattering band assigned to amorphous properties in its X-ray diffractometry using CuK α rays. The results obtained are shown in Table D-4.

TABLE D-4

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	SnO ₂	443	3.48	85
2	SnO	483	3.53	73

It is apparent that the use of the tin compound oxide according to the present invention as a negative electrode active material provides a battery superior to that using SnO_2 or SnO in terms of charge and discharge cycle characteristics and capacity.

5 COMPARATIVE EXAMPLE D-2

A coin battery was prepared and tested in the same manner as in Example D-1, except for using, as a negative electrode active material, Fe_2O_3 , amorphous V_2O_5 , or LiCoVO_4 . The results obtained are shown in Table D-5.

10 TABLE D-5

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	Fe_2O_3	109	3.16	13
2	V_2O_5	82	2.83	82
3	LiCoO_4	256	2.91	102

It is seen that the battery using the tin compound oxide according to the present invention as a negative electrode active material is superior to that using Fe_2O_3 , amorphous V_2O_5 , or LiCoVO_4 in terms of charge and discharge cycle characteristics, discharge potential, and discharge capacity.

EXAMPLE D-4

25 A coin nonaqueous secondary battery was prepared and tested in the same manner as in Run No. 1 of Example D-1, except for replacing LiCoO_2 with each of the positive electrode active materials shown in Table D-6. The results obtained are shown in Table D-6.

30 TABLE D-6

Run No.	Positive Electrode Active Material	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	LiCoO_2	493	3.5	335
2	LiNiO_2	497	3.39	340
3	$\text{LiCo}_{0.95}\text{V}_{0.05}\text{O}_{2.0}$	485	3.49	390
4	LiMn_2O_4	474	3.54	329
5	LiMnO_2	505	3.31	330

It is seen that the negative electrode active material of the present invention provides a nonaqueous secondary battery excellent in all of charge and discharge cycle characteristics, discharge potential, and discharge capacity regardless of which of these positive electrode active materials is used.

EXAMPLE D-5

45 A mixture of 86% of compound D-1-A synthesized in Synthesis Example D-1 as a negative electrode active material, 6% of flake graphite, and 3% of acetylene black was mixed with 4% of an aqueous dispersion of a styrene-butadiene rubber and 1% of carboxymethyl cellulose as binders. The mixture was kneaded together with water to prepare a slurry. The slurry was extrusion coated on both sides of a 18 μm thick copper foil and, after drying, compressed by calendaring. The compressed sheet was cut to a prescribed size to prepare a 124 μm thick negative electrode sheet.

50 A mixture of 87% of LiCoO_2 as a positive electrode active material, 6% of flake graphite, 3% of acetylene black, and, as binders, 3% of an aqueous dispersion of polytetrafluoroethylene and 1% of sodium polyacrylate was kneaded with water, and the resulting slurry was applied on both sides of a 20 μm thick aluminum foil, dried, compressed, and cut to size in the same manner as described above to prepare a 220 μm thick positive electrode sheet.

A nickel or aluminum lead was connected by spot welding to the end of the negative electrode sheet or the positive electrode sheet, respectively. Both the electrode sheets with a lead were dried at 150 °C for 2

hours in dry air having a dew point of not higher than -40°C .

Dried positive electrode sheet (8), finely porous polypropylene film separator (Cell Guard 2400) (10), dried negative electrode sheet (9), and separator (10) were laminated in this order and rolled up by means of a winder.

5 The roll was put in cylindrical open-top battery case (11) made of nickel-plated iron which also served as a negative electrode terminal, and a 1 mol/l LiPF_6 solution in a 2:2:6 (by volume) mixture of ethylene carbonate, butylene carbonate, and dimethyl carbonate was poured into the case. Battery cover (12) with a positive electrode terminal was fitted into the top of case (11) via gasket (13) to prepare a cylindrical battery. Positive electrode terminal (12) and positive electrode sheet (8) were previously connected via a
10 lead terminal, and battery case (11) and negative electrode sheet (9) were connected in the same way.

The cross section of the thus assembled cylindrical battery is shown in Fig. 3. Numeral (14) is a safety valve. The resulting battery was tested in the same manner as in Example D-1. The results obtained are shown in Table D-7. In Table D-7, symbol (e) means a discharge capacity per ml of a C size battery.

15

TABLE D-7

Run No.	(b) (mAh/g)	(c) (V)	(d) (cycles)	(e) (mAh/ml)
1	498	3.56	570	366

20

EXAMPLE D-6 AND COMPARATIVE EXAMPLE D-3

25 Fifty coin batteries were prepared in the same manner as in Example D-1 using each of compounds D-1-A to Q synthesized in Synthesis Example D-1, compounds D-4-A to F synthesized in Synthesis Example D-4, and compound D-5-A to P synthesized in Synthesis Example D-5 as a negative electrode active material and subjected to a safety test in the same manner as in Example A-7. As a result none of them ignited.

30 For comparison, the same test was conducted, except for using a pellet (15 mm in diameter; 100 mg in weight) of an Li-Al (80%-20%) alloy as a negative electrode active material. As a result, 32 out of 50 ignited.

It can be seen from these results that the nonaqueous secondary battery according to the present invention are of high safety.

35 COMPARATIVE EXAMPLE D-4

SnSiO_3 (compound D-1-A) synthesized in Synthesis Example D-1 was heat treated at 700°C for 2 hours and cooled to room temperature to obtain crystalline SnSiO_3 . The X-ray diffraction pattern of the product showed no peak assigned to amorphous properties. A coin battery was prepared and tested in the
40 same manner as in Example D-1, except for using the thus prepared crystalline SnSiO_3 as a negative electrode active material. The results of the charge and discharge test are shown in Table D-8.

TABLE D-8

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	SnSiO_3 (crystalline)	441	3.48	95

45 It can be seen that the nonaqueous secondary battery prepared by using the amorphous tin compound oxide of the present invention as a negative electrode active material is superior in charge and discharge cycle characteristics and capacity to that prepared by using a crystalline tin compound oxide.

EXAMPLE D-7

55 A coin battery was prepared and tested in the same manner as in Run No. 1 of Example D-1, except for replacing compound D-1-A as a negative electrode active material with each of compounds D-4-A to F synthesized in Synthesis Example D-4 and compounds D-5-A to P synthesized in Synthesis Example D-5. The results of the charge and discharge test are shown in Table D-9.

TABLE D-9

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	D-4-A	500	3.50	350
2	D-4-B	495	3.51	344
3	D-4-C	515	3.51	367
4	D-4-D	516	3.50	359
5	D-4-E	510	3.49	348
6	D-4-F	520	3.53	370
7	D-5-A	540	3.51	376
8	D-5-B	545	3.48	374
9	D-5-C	535	3.51	378
10	D-5-D	540	3.52	374
11	D-5-E	545	3.51	385
12	D-5-F	550	3.52	390
13	D-5-G	555	3.51	365
14	D-5-H	557	3.51	368
15	D-5-I	548	3.52	388
16	D-5-J	510	3.52	354
17	D-5-K	555	3.52	378
18	D-5-L	550	3.51	355
19	D-5-M	560	3.51	387
20	D-5-N	558	3.51	373
21	D-5-O	557	3.51	383
22	D-5-P	562	3.52	372

The results prove that the negative electrode active materials which can be used in the present invention provide a nonaqueous secondary battery with excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity. It is also seen that batteries using a P-containing compound as a negative electrode active material are particularly excellent in charge and discharge cycle characteristics.

EXAMPLE D-8

A coin battery was prepared and tested in the same manner as in Example D-4, except for replacing compound D-1-A as a negative electrode active material with each of compounds D-4-A to F synthesized in Synthesis Example D-4 and compounds D-5-A to P synthesized in Synthesis Example D-5. The results of the charge and discharge test are shown in Table D-10. In Table D-10, symbol (e) has the same meaning as in Table D-7.

TABLE D-10

	Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)	(e) (mAh/ml)
5	1	D-4-A	502	3.56	570	368
	2	D-4-B	498	3.57	560	366
	3	D-4-C	518	3.57	575	381
	4	D-4-D	518	3.55	580	380
	5	D-4-E	511	3.55	568	376
10	6	D-4-F	522	3.57	581	381
	7	D-5-A	543	3.58	580	399
	8	D-5-B	549	3.54	581	403
	9	D-5-C	540	3.57	584	397
	10	D-5-D	543	3.58	582	399
15	11	D-5-E	551	3.56	591	405
	12	D-5-F	553	3.56	593	406
	13	D-5-G	560	3.56	574	412
	14	D-5-H	562	3.57	577	413
	15	D-5-I	553	3.57	595	406
20	16	D-5-J	512	3.57	573	376
	17	D-5-K	557	3.56	592	409
	18	D-5-L	553	3.56	570	406
	19	D-5-M	562	3.55	596	413
	20	D-5-N	560	3.56	590	412
25	21	D-5-O	559	3.56	594	411
	22	D-5-P	561	3.56	584	413

As described above, the use of an Li-containing transition metal oxide as a positive electrode active material and at least one specific compound oxide as a negative electrode active material affords a nonaqueous secondary battery having a high discharge potential, a high discharge capacity and excellent charge and discharge cycle characteristics.

SnO, GeO₂, and PbO₂ used in the following Examples are commercially available ones.

SYNTHESIS EXAMPLE E-1

A uniform mixture of SnO and SnF₂ at a molar ratio of 0.9:0.1, totally weighing 20 g, was calcined in an argon atmosphere at 950 °C for 6 hours and cooled to room temperature over a period of 2 hours to obtain SnF_{0.2}O_{0.9}. The calcined product was ground in a grinding machine and sieved to obtain a powdered negative electrode active material precursor having an average particle size of about 10 μm.

SYNTHESIS EXAMPLE E-2

A uniform mixture of SnO, SiO₂, and SnF₂ at a molar ratio of 0.8:1.0:0.2, totally weighing 20 g, was calcined in an argon atmosphere at 1000 °C for 6 hours and cooled to room temperature over a period of 2 hours to obtain glassy amorphous SnSiF_{0.4}O_{2.8} as a yellow solid. The calcined product was ground in a grinding machine and sieved to obtain a powdered negative electrode active material precursor having an average particle size of about 5 μm.

Alternatively, a 5% acidic aqueous solution containing SnCl₂ and SiCl₄ at a molar ratio of 0.8:1.0 was neutralized with aqueous ammonia while stirring. The stirring was continued for an additional period of 4 hours while keeping at 80 to 90 °C, and the thus formed precipitate was collected by filtration and dried in vacuo at 200 °C for 24 hours to obtain Sn_{0.8}SiO_{2.8} as a yellow powder. The powder was mixed with SnF₂ at a molar ratio of 1:0.2. A 20 g portion of the mixture was heat treated at 1000 °C for 1 hour in an argon atmosphere to obtain glassy amorphous SnSiF_{0.4}O_{2.8} as a yellow solid.

SYNTHESIS EXAMPLE E-3

A uniform mixture of SnO, SiO₂, SnF₂, and GeO₂ at a molar ratio of 0.8:1.0:0.2:0.1, totally weighing 20 g, was calcined in an argon atmosphere at 1000 °C for 6 hours and cooled to room temperature over a

period of 2 hours to obtain glassy amorphous $\text{SnSiGe}_{0.1}\text{F}_{0.4}\text{O}_{3.0}$ as a yellow solid. The calcined product was ground in a grinding machine and sieved to obtain a powdered negative electrode active material precursor having an average particle size of about 6 μm . In the same manner as described above but using stoichiometrical amounts of the respective raw materials, $\text{SnSiTi}_{0.1}\text{F}_{0.4}\text{O}_{3.0}$, $\text{SnSiAl}_{0.1}\text{F}_{0.4}\text{O}_{3.0}$, $\text{SnSiFe}_{0.1}\text{F}_{0.4}\text{O}_{3.0}$, and $\text{SnSiZn}_{0.1}\text{F}_{0.4}\text{O}_{3.0}$ were synthesized.

SYNTHESIS EXAMPLE E-4

A uniform mixture of SnO , GeO_2 , and SnF_2 at a molar ratio of 0.8:1.0:0.2, totally weighing 20 g, was calcined in an argon atmosphere at 1000 °C for 6 hours and cooled to room temperature over a period of 2 hours to obtain glassy amorphous $\text{SnGeF}_{0.4}\text{O}_{2.8}$ as a yellow solid. The calcined product was ground in a grinding machine and sieved to obtain a powdered negative electrode active material precursor having an average particle size of about 4 μm .

SYNTHESIS EXAMPLE E-5

A uniform mixture of SnO , PbO_2 , and SnF_2 at a molar ratio of 0.8:1.0:0.2, totally weighing 20 g, was calcined in an argon atmosphere at 1000 °C for 6 hours and cooled to room temperature over a period of 2 hours to obtain an amorphous solid, $\text{SnPbF}_{0.4}\text{O}_{2.8}$. The calcined product was ground in a grinding machine and sieved to obtain a powdered negative electrode active material precursor having an average particle size of about 8 μm .

SYNTHESIS EXAMPLE E-6

A dry mixture of 2.26 g of lithium carbonate, 5.0 g of tricobalt tetroxide, and 0.16 g of zirconium dioxide was calcined in air at 900 °C for 18 hours to synthesize crystalline $\text{LiCoZr}_{0.02}\text{O}_2$ as a positive electrode active material. The resulting product was ground to obtain a brown powder having an average particle size of 5 μm .

SYNTHESIS EXAMPLE E-7

A dry mixture of 1.20 g of lithium carbonate and 5.92 g of manganese dioxide was calcined in air at 800 °C for 12 hours to synthesize crystalline LiMn_2O_4 as a positive electrode active material. Average particle size: 3 μm .

EXAMPLE E-1

Electrode:

A negative electrode active material mixture consisting of 82% of each of the negative electrode active material precursors shown in Table E-1, 8% of flake graphite and 4% of acetylene black as conducting agents, and 6% of polyvinylidene fluoride as a binder was compression molded into a pellet of 13 mm in diameter and 22 mg in weight. For comparative negative electrode active materials, coke (LCP-u, produced by Nippon Steel Chemical Co., Ltd.) and rutile type WO_2 were used.

Counter Electrode:

A positive electrode active material mixture consisting of 82% of each of the positive electrode active materials shown in Table E-1, 8% of flake graphite, 4% of acetylene black, and 6% of tetrafluoroethylene was compression molded to obtain a pellet of 13 mm in diameter and 110 mg in weight.

The negative electrode pellet and the positive electrode pellet were dried in a dry box (dry air; dew point: -40 to -70 °C) at 150 °C for about 3 hours by means of a far infrared heater.

Collector:

A 80 μm thick net of SUS316 was welded to each of a positive case and a negative case.

Electrolytic Solution:

200 μl of a 1 mol/l solution of LiPF_6 in a 2:2:6 (by volume) mixed solvent of ethylene carbonate, butylene carbonate and dimethyl carbonate.

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Separator:

A finely porous polypropylene sheet and polypropylene nonwoven fabric impregnated with the electrolytic solution.

10 The positive electrode case and the negative electrode case were fitted to each other to prepare a coin lithium battery.

The resulting coin battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm², a cut-off voltage of 4.3 V in charging, and a cut-off voltage of 2.7 V in discharging. All the tests were started with lithium intercalation into the negative electrode active material precursor. While more than 50 kinds of coin batteries were prepared and tested using a variety of combinations of a negative electrode active material and a positive electrode active material, only the typical results are shown in Table E-1. It should therefore be understood that the combination of a negative electrode active material and a positive electrode active material which can be used in the present invention is not limited to those shown in Table E-1.

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TABLE E-1

	Positive Electrode Active Material	Negative Electrode Active Material	Average Discharge Potential (V)	Discharge Capacity at the 2nd Cycle (mAh/g)	Cycle Charac- teristics*
5					
10	Comparison:				
	$\text{LiCoZr}_{0.02}\text{O}_2$	coke	3.40	180	0.10
	$\text{LiCoZr}_{0.02}\text{O}_2$	WO_2	3.20	160	0.15
15	LiMn_2O_4	coke	3.30	170	0.12
	LiMn_2O_4	WO_2	3.10	140	0.17
	Invention:				
20	$\text{LiCoZr}_{0.02}\text{O}_2$	$\text{SnF}_{0.2}\text{O}_{0.9}$	3.53	450	0.07
	$\text{LiCoZr}_{0.02}\text{O}_2$	$\text{SnSiF}_{0.4}\text{O}_{2.8}$	3.55	420	0.04
25	$\text{LiCoZr}_{0.02}\text{O}_2$	$\text{SnSiF}_{1.0}\text{O}_{2.5}$	3.55	410	0.05
	$\text{LiCoZr}_{0.02}\text{O}_2$	$\text{SnSiGe}_{0.1}\text{F}_{0.4}\text{O}_3$	3.56	430	0.04
	$\text{LiCoZr}_{0.02}\text{O}_2$	$\text{SnSiAl}_{0.1}\text{F}_{0.4}\text{O}_3$	3.56	420	0.03
30	$\text{LiCoZr}_{0.02}\text{O}_2$	$\text{SnSiTi}_{0.1}\text{F}_{0.4}\text{O}_3$	3.56	420	0.03
	$\text{LiCoZr}_{0.02}\text{O}_2$	$\text{SnSiZn}_{0.1}\text{F}_{0.4}\text{O}_3$	3.55	410	0.04
	$\text{LiCoZr}_{0.02}\text{O}_2$	$\text{SnSiFe}_{0.1}\text{F}_{0.4}\text{O}_3$	3.54	410	0.05
35	$\text{LiCoZr}_{0.02}\text{O}_3$	$\text{SnGeF}_{0.4}\text{O}_{2.8}$	3.50	450	0.06
	$\text{LiCoZr}_{0.02}\text{O}_3$	$\text{SnPbF}_{0.4}\text{O}_{2.8}$	3.50	400	0.08
40	LiMn_2O_4	$\text{SnF}_{0.2}\text{O}_{0.9}$	3.50	430	0.08
	LiMn_2O_4	$\text{SnSiF}_{0.4}\text{O}_{2.8}$	3.51	400	0.07
	LiMn_2O_4	$\text{SnSiGe}_{0.1}\text{F}_{0.4}\text{O}_3$	3.51	400	0.08
45	LiMn_2O_4	$\text{SnSiAl}_{0.1}\text{F}_{0.4}\text{O}_3$	3.52	410	0.05
	LiMn_2O_4	$\text{SnSiTi}_{0.1}\text{F}_{0.4}\text{O}_3$	3.52	400	0.05

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LiMn_2O_4	$\text{SnGeF}_{0.4}\text{O}_{2.8}$	3.45	420	0.08
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Note: * (Discharge capacity of the 10th cycle - discharge capacity of the 1st cycle)/discharge capacity of the 1st cycle

It is obvious from the results in Table E-1 that the nonaqueous secondary batteries using the negative electrode active material according to the present invention are superior in discharge capacity and cycle characteristics to those using conventional negative electrode active materials.

According to the present invention, the use of an oxide containing the group IIIB, IVB or VB metal and fluorine furnishes a nonaqueous secondary battery having a high discharge capacity and satisfactory charge and discharge cycle characteristics.

Compared with the conventional batteries using coke or WO_2 as a negative electrode active material, the nonaqueous secondary batteries of the present invention have a higher average discharge potential by 0.1 to 0.35 V. Further, the discharge capacity, measured at the 2nd cycle, of the batteries of the present invention is at least double that of the conventional ones. Therefore, the batteries of the present invention are very effective in the applications requiring high power.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

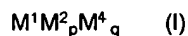
Claims

1. A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt, wherein said negative electrode active material contains at least one compound capable of intercalating and deintercalating lithium mainly comprising an atom of the group IIIB, IVB or VB of the periodic table.
2. A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt, wherein said negative electrode active material mainly comprises an amorphous compound containing at least two atoms selected from the elements of the groups IIIB, IVB, and VB of the periodic table.
3. A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt, wherein said negative electrode active material is a compound capable of intercalating and deintercalating lithium containing at least one of the atoms of the group IIIB, IVB, and VB of the periodic table and fluorine.
4. A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt, wherein said negative electrode active material contains at least one compound of the atom of the group IIIB, IVB or VB of the periodic table, Zn, or Mg which is capable of intercalating and deintercalating lithium.
5. A nonaqueous secondary battery as claimed in claims 1 to 4, wherein the atom of the group IIIB, IVB and VB of the periodic table is selected from the group consisting of AL, Si, Ge, Sn, Pb, As, and Sb.
6. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material is a compound which is amorphous at the time of intercalating lithium ion.
7. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material is a compound which is amorphous at the time of assembling a battery.
8. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material mainly comprises a compound represented by formula (I):



wherein M^1 and M^2 , which are different from each other, each represent at least one of Si, Ge, Sn, Pb, P, B, Al, As, and Sb; M^4 represents at least one of O, S, Se, and Te; p represents a number of from 0.001 to 10; and q represents a number of from 1.00 to 50.

9. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material mainly comprises a compound represented by formula (I):



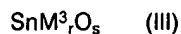
wherein M^1 and M^2 are different from each other, M^1 represents at least one of Ge, Sn, Pb, Sb, and Bi; M^2 represents at least atom of the groups IIIB, IVB, and VB of the periodic table; M^4 represents at least one of O, S, Se, and Te; p represents a number of from 0.001 to 1; and q represents a number of from 1.00 to 50.

10. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material mainly comprises a compound represented by formula (II):



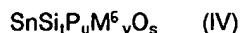
wherein M^3 represents at least one of Si, Ge, Pb, P, B, Al, As, and Sb; M^5 represents at least one of O and S; p represents a number of from 0.001 to 10; and q represents a number of from 1.00 to 50.

11. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material mainly comprises a compound oxide represented by formula (III):



wherein M^3 represents at least one of Si, Ge, Pb, P, B, Al, and As; r represents a number of from 0.01 to 5.0; and s represents a number of from 1.0 to 26.

12. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material mainly comprises a compound oxide represented by formula (IV):



M^6 represents at least one of Ge, B, Al, and Pb; t represents a number of from 0.01 to 2.0; u represents a number of from 0.01 to 4.0; v represents a number of from 0.01 to 2.0; and s represents a number of from 1.0 to 26.

13. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material mainly comprises a compound oxide represented by formula (V):



wherein M^7 represents at least one of Ge, B, and Pb; t represents a number of from 0.01 to 2.0; u represents a number of from 0.01 to 4.0; v represents a number of from 0 to 2.0; w represents a number of from 0.01 to 2.0; and s represents a number of from 1.0 to 26.

14. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material is obtained by a calcination method consisting of heating at a rate of temperature rise of 4° to $2000^\circ\text{C}/\text{min}$, maintaining at 250° to 1500°C for 0.01 to 100 hours, and cooling at a rate of temperature drop of 2° to $10^7^\circ\text{C}/\text{min}$.

15. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said negative electrode active material is obtained by a calcination method consisting of heating at a rate of temperature rise of 10° to 2000°C/min , maintaining at 250° to 1500°C for 0.01 to 100 hours, and cooling at a rate of temperature drop of 2° to 10^7°C/min .

16. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said positive electrode active material is a lithium-containing transition metal oxide.

17. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said positive electrode active contains at least one compound represented by formula Li_xQO_y , wherein Q represents at least one transition metal selected from Co, Mn, Ni, V, and Fe; x is from 0.2 to 1.2; and y is from 1.4 to 3.

18. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said positive electrode active contains at least one compound selected from Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{Fe}_{1-b}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Co}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Ni}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{V}_{2-c}\text{O}_4$, and $\text{Li}_x\text{Mn}_c\text{Fe}_{2-c}\text{O}_4$ (wherein $x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.8$ to 0.98 ; $c = 1.6$ to 1.96 ; $z = 2.01$ to 2.3).

19. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein said positive electrode active material is a lithium-containing manganese compound having a spinel structure and a stoichiometric or non-stoichiometric composition.

20. A nonaqueous secondary battery as claimed in any of claims 1 to 4, wherein lithium is intercalated in an amount of from 1 to 20 equivalents.

FIG. 1

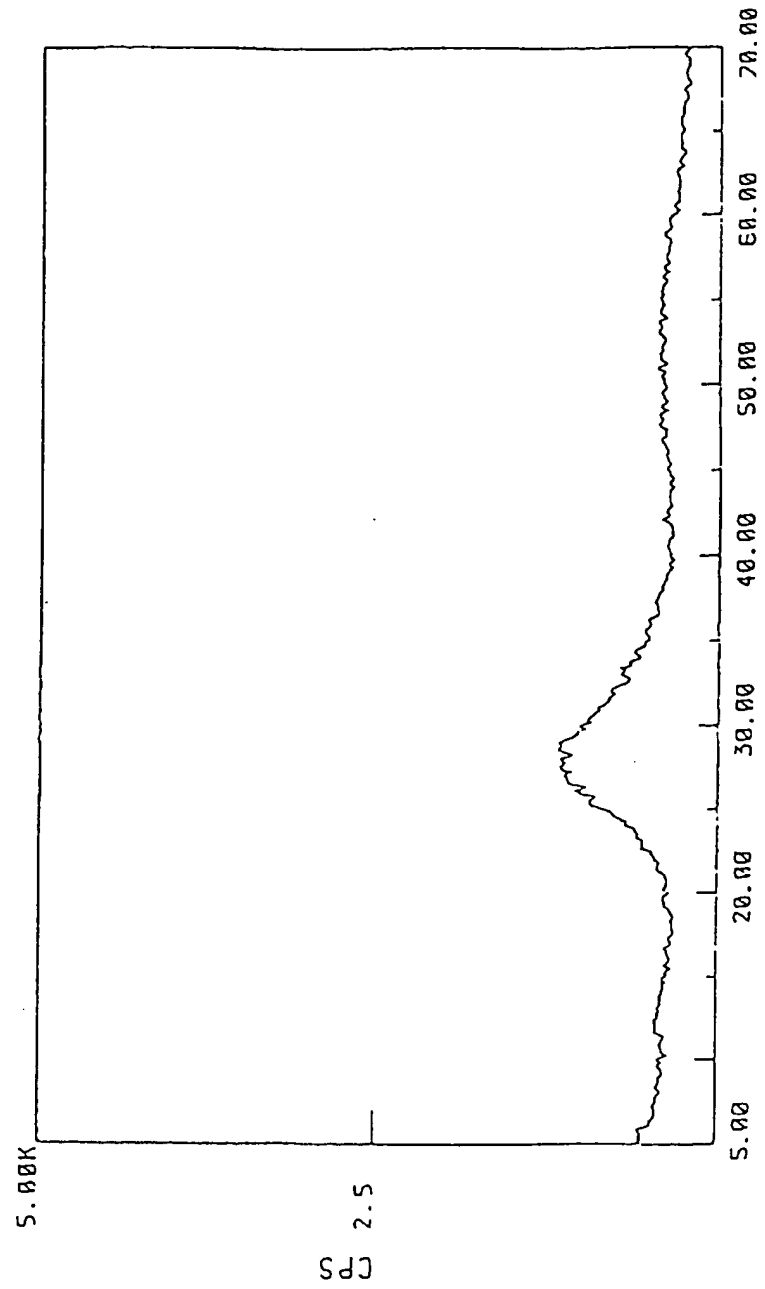


FIG. 2

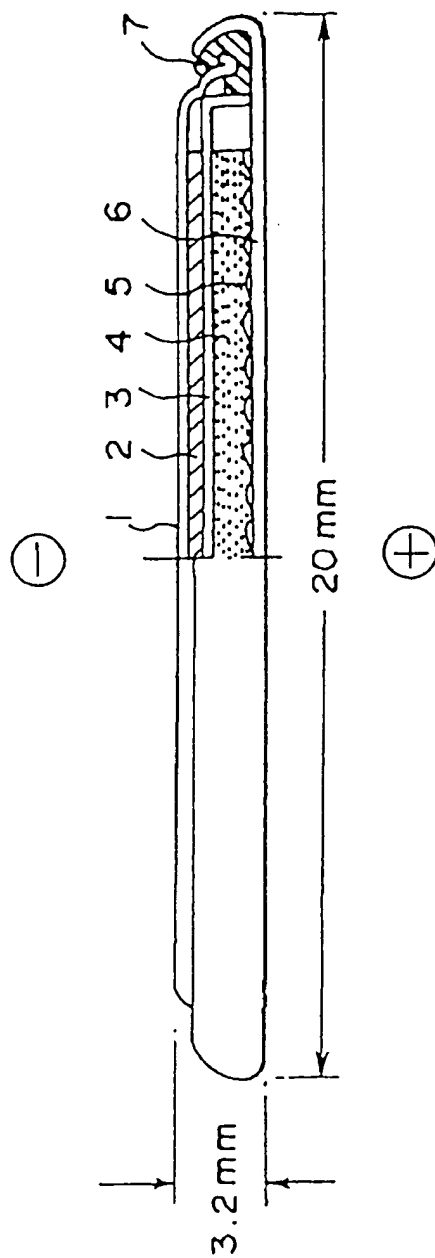
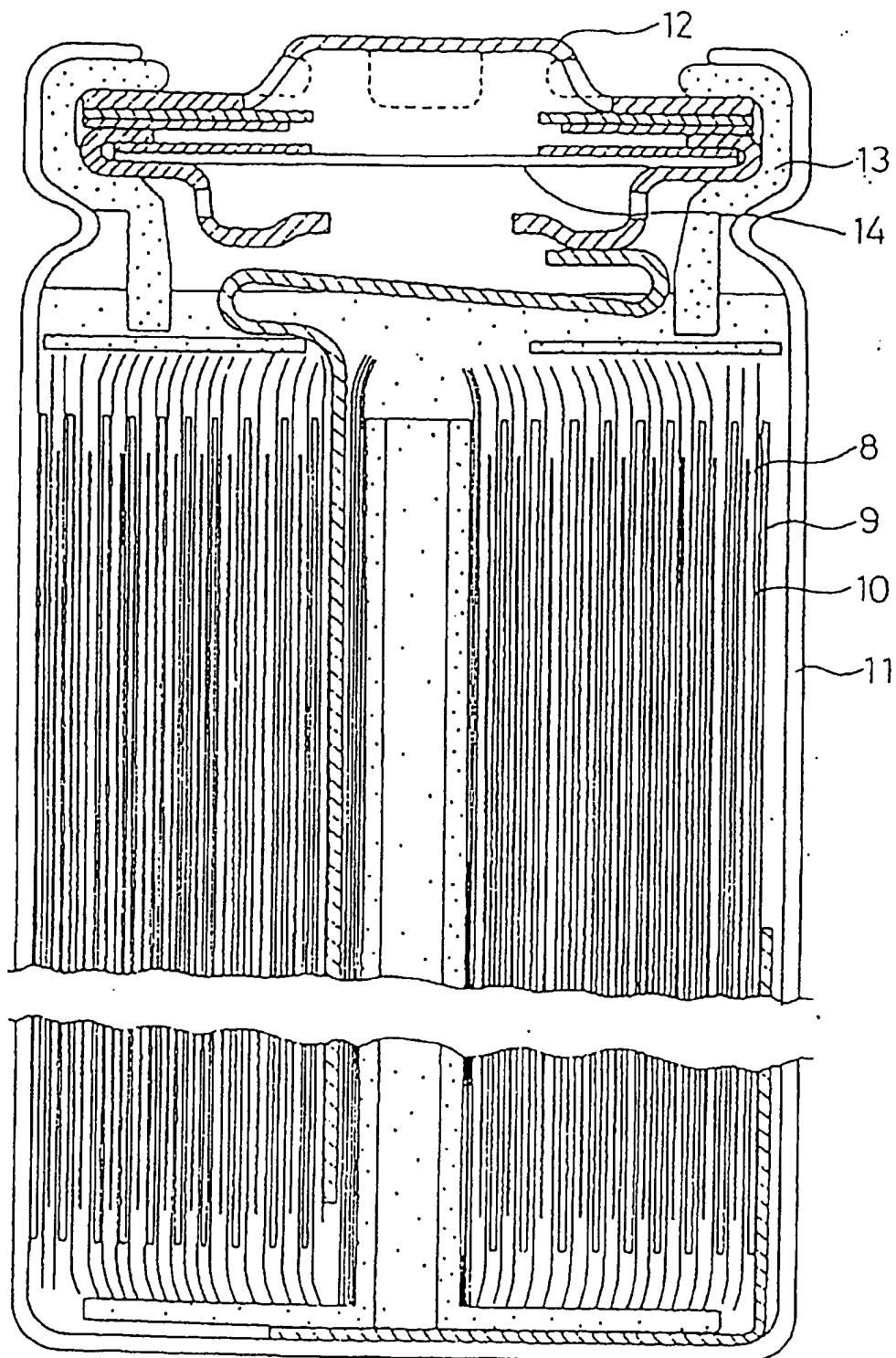


FIG. 3





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 6643

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	EP-A-0 615 296 (SEIKO ELECTRONIC COMPONENTS) * page 3, line 20 - line 21 * * page 7, line 20 - line 30 * * page 5, line 39 - line 42; claims 1,5 * ---	2,4-11, 16-19	H01M4/48 H01M4/58
P,X	EP-A-0 582 173 (SEIKO ELECTRONIC INSTRUMENTS) * claims 1,3,4 * ---	1,4-7,20	
X	PROCEEDINGS OF THE SYMPOSIUM ON HIGH POWER, AMBIENT TEMPERATURE LITHIUM BATTERIES. PHOENIX, ARIZONA, OCT. 13-17 1991. THE ELECTROCHEMICAL SOCIETY INC., PENNINGTON, NJ, USA, vol.92-15 pages 101 - 112 MASAYUKI MORITA ET AL 'Layered-Structure BC2N as a Negative Electrode Matrix for Rechargeable Lithium Batteries' * abstract * -----	2,4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 February 1995	Examiner Andrews, M
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	